# Bohr's atomic model

(1) This model was based on the quantum theory of radiation and the classical law of physics. It gave new idea of atomic structure in order to explain the stability of the atom and emission of sharp spectral lines.

(2) ***Postulates*** of this theory are:

(i) The atom has a central massive core nucleus where all the protons and neutrons are present. The size of the nucleus is very small.

(ii) The electron in an atom revolves around the nucleus in certain discrete orbits. Such orbits are known as *stable orbits* or *non – radiating* or *stationary orbits*.

(iii) The force of attraction between the nucleus and the electron is equal to centrifugal force of the moving electron.

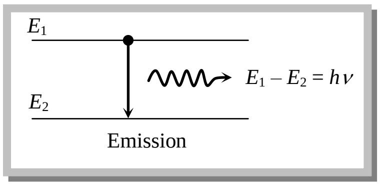
**Force of attraction towards nucleus = centrifugal force**

(iv) An electron can move only in those permissive orbits in which the angular momentum (mvr) of the electron is an integral multiple of $h/2\pi$. Thus, $\text{mvr} = n\frac{\text{h}}{2\pi}$

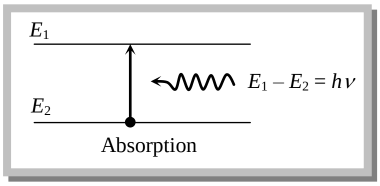
Where, $m$ = mass of the electron, $r$ = radius of the electronic orbit, v = velocity of the electron in its orbit.

(v) The angular momentum can be $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}, ......\frac{nh}{2\pi}$. This principal is known as ***quantization of angular momentum***. In the above equation 'n' is any integer which has been called as *principal quantum number*. It can have the values $n$=1,2,3, ------- (from the nucleus). Various energy levels are designed as $K(n=1)$, $L(n=2)$, $M(n=3)$ ------- etc. Since the electron present in these orbits is associated with some energy, these orbits are called energy levels.

(vi) The emission or absorption of radiation by the atom takes place when an electron jumps from one stationary orbit to another.



Emission



Absorption

(vii) The radiation is emitted or absorbed as a single quantum (photon) whose energy $h\nu$ is equal to the difference in energy $\Delta E$ of the electron in the two orbits involved. Thus, $h\nu = \Delta E$

Where '$h$' =Planck's constant, $\nu$ =frequency of the radiant energy. Hence the spectrum of the atom will have certain fixed frequency.

(viii) The lowest energy state ($n$=1) is called the *ground state*. When an electron absorbs energy, it gets excited and jumps to an outer orbit. It has to fall back to a lower orbit with the release of energy.

(3) **Advantages of Bohr's theory**

(i) Bohr's theory satisfactorily explains the spectra of species having one electron, *viz.* hydrogen atom, $He^{+}, Li^{2+}$ etc.

(ii) *Calculation of radius of Bohr's orbit*: According to Bohr, radius of orbit in which electron moves is

$$\boxed{r = \left[\frac{h^2}{4\pi^2 me^2 k}\right] . \frac{n^2}{Z}}$$

Where, $n$ =Orbit number, $m$ =Mass number $\left[9.1 \times 10^{-31} kg\right]$, e =Charge on the electron $\left[1.6 \times 10^{-19}\right]$

Z =Atomic number of element, $k$ = Coulombic constant $\left[9 \times 10^{9}\ Nm^2 c^{-2}\right]$

After putting the values of $m,e,k,h$, we get.

$$\boxed{r_n = \frac{n^2}{Z} \times 0.529\ \text{Å} \ or\ r_n = \frac{n^2}{Z} \times 0.529\ nm}$$

(a) For a particular system [e.g., *H, He*$^+$ or *Li*$^{+2}$]

$r \propto n^2$ [Z = constant]

Thus we have $\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2}$ i.e., $r_1 : r_2 : r_3 .........\ :: 1 : 4 : 9.......\ r_1 < r_2 < r_3$

(b) For particular orbit of different species

$r \propto \frac{1}{Z}$ [Z =constant] Considering *A* and *B* species, we have $\frac{r_A}{r_B} = \frac{Z_B}{Z_A}$

Thus, radius of the first orbit *H*, $He^+, Li^{+2}$ and $Be^{+3}$ follows the order: $H > He^+ > Li^{+2} > Be^{+3}$

(iii) *Calculation of velocity of electron*

$$\boxed{V_n = \frac{2\pi e^2 ZK}{nh}, V_n = \left[\frac{Ze^2}{mr}\right]^{1/2}}$$

For *H* atom, $V_n = \frac{2.188 \times 10^8}{n} cm.\sec^{-1}$

(a) For a particular system [*H, He*$^+$ or *Li*$^{+2}$]

$\mathrm{V} \propto \frac{1}{\mathrm{n}}$ [Z = constant] Thus, we have, $\frac{V_1}{V_2} = \frac{n_2}{n_1}$

The order of velocity is $V_1 > V_2 > V_3 .........$ or $V_1 : V_2 : V_3 ..........\ :: 1 : \frac{1}{2} : \frac{1}{3} ........$

(b) For a particular orbit of different species

$V \propto Z$ [n =constant] Thus, we have $H < He^+ < Li^{+2}$

(c) For *H or He*$^+$ or *Li*$^{+2}$, we have

$V_1 : V_2 = 2 : 1;\ V_1 : V_3 = 3 : 1;\ V_1 : V_4 = 4 : 1$

(iv) *Calculation of energy of electron in Bohr's orbit*

Total energy of electron = K.E. + P.E. of electron $= \frac{kZe^2}{2r} - \frac{kZe^2}{r} = -\frac{kZe^2}{2r}$

Substituting of *r*, gives us $E = \frac{-2\pi^2 mZ^2 e^4 k^2}{n^2 h^2}$ Where, n=1, 2, 3.........∞

Putting the value of m, e, k, h, $\pi$ we get

$$E = 21.8 \times 10^{-12} \times \frac{Z^2}{n^2} erg\ per\ atom = -21.8 \times 10^{-19} \times \frac{Z^2}{n^2} J\ per\ atom\ (1J = 10^7 erg)$$

$$E = -13.6 \times \frac{Z^2}{n^2} eV\ per\ atom (1\text{eV} = 1.6 \times 10^{-19}\ J) = -313.6 \times \frac{Z^2}{n^2} kcal./mole \quad (1\ cal = 4.18J)$$

or $\frac{-1312}{n^2} Z^2 kJmol^{-1}$

(a) For a particular system[*H, He*$^+$ or *Li*$^{+2}$]

$E \propto -\frac{1}{n^2}$ [Z =constant] Thus, we have $\frac{E_1}{E_2} = \frac{n_2^2}{n_1^2}$

The energy increase as the value of *n* increases

(b) For a particular orbit of different species

$E \propto -Z^2$ [*n* =constant] Thus, we have $\frac{E_A}{E_B} = \frac{Z_A^2}{Z_B^2}$

For the system *H, He*$^+$ , *Li*$^{+2}$, *Be*$^{+3}$ (n-same) the energy order is $H > He^+ > Li^{+2} > Be^{+3}$

The energy decreases as the value of atomic number Z increases.

When an electron jumps from an outer orbit (higher energy) $n_2$ to an inner orbit (lower energy) $n_1$, then the energy emitted in form of radiation is given by

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2 k^2 me^4 Z^2}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \Rightarrow \Delta E = 13.6 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) eV / atom$$

As we know that $E = h\bar{\nu},\ c = \nu\lambda$ and $\bar{\nu} = \frac{1}{\lambda} = \frac{\Delta E}{hc},\ = \frac{2\pi^2 k^2 me^4 Z^2}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

This can be represented as $\frac{1}{\lambda} = \bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ where, $R = \frac{2\pi^2 k^2 me^4}{ch^3}$ $R$ is known as Rydberg constant. Its value to be used is 109678 $cm^{-1}$.

(4) **Quantisation of energy of electron**

(i) *In ground state*: No energy emission. In ground state energy of atom is minimum and for 1st orbit of H-atom, $n = 1$.

$\therefore E_1 = -13.6 eV$.

(ii) *In excited state*: Energy levels greater than $n_1$ are excited state. i.e. for H- atom $n_2, n_3, n_4$ are excited state. For *H*- atom first excitation state is $= n_2$

(iii) *Excitation potential*: Energy required to excite electron from ground state to any excited state.

$$\text{Ground state} \longrightarrow \text{Excited state}$$

Ist excitation potential $= E_2 - E_1 = -3.4 + 13.6 = 10.2\ eV$.

IInd excitation potential $= E_3 - E_1 = -1.5 + 13.6 = 12.1\ eV$.

(iv) *Ionisation energy* : The minimum energy required to relieve the electron from the binding of nucleus.

$$\boxed{E_{\text{ionisation}} = E_\infty - E_n = +13.6 \frac{Z_{\text{eff.}}^2}{n^2} eV.}$$

(v) *Ionisation potential* : $V_{\text{ionisation}} = \frac{E_{ionisation}}{e}$

(vi) *Separation energy* : Energy required to excite an electron from excited state to infinity.

$$\text{S.E.} = E_\infty - E_{excited}\ .$$

(vii) *Binding energy* : Energy released in bringing the electron from infinite to any orbit is called its binding energy (B.E.).

Note : ❑ Principal Quantum Number '$n$' $= \sqrt{\frac{13.6}{(B.E.)}}$ .

(5) **Spectral evidence for quantisation** (Explanation for hydrogen spectrum on the basis of bohr atomic model)

(i) The light absorbed or emitted as a result of an electron changing orbits produces characteristic absorption or emission spectra which can be recorded on the photographic plates as a series of lines, the optical spectrum of hydrogen consists of several series of lines called **Lyman, Balmar, Paschen, Brackett, Pfund** and **Humphrey.** These spectral series were named by the name of scientist who discovered them.

(ii) To evaluate wavelength of various H-lines Ritz introduced the following expression,

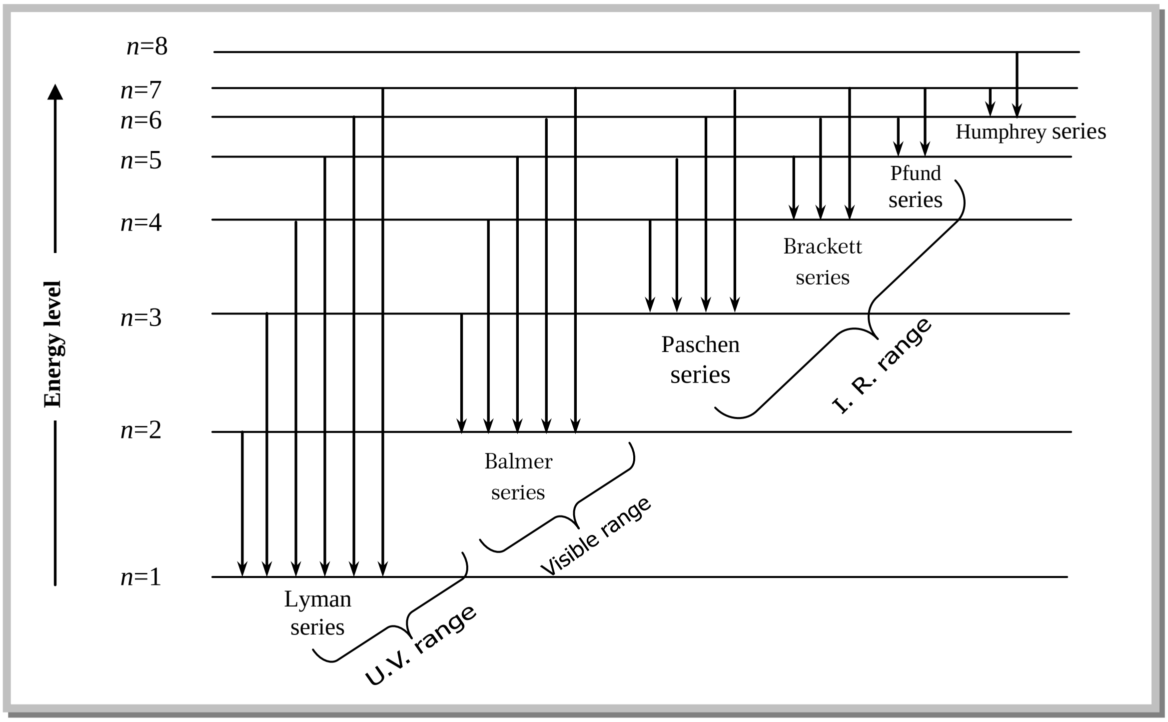
$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where, R is $= \frac{2\pi^2 me^4}{ch^3} =$ Rydberg's constant

It's theoritical value = 109,737 $cm^{-1}$ and It's experimental value = $109{,}677.581 cm^{-1}$

This remarkable agreement between the theoretical and experimental value was great achievment of the Bohr model.

(iii) Although H- atom consists only one electron yet it's spectra consist of many spectral lines as shown in fig.



(iv) *Comparative study of important spectral series of Hydrogen*

| S.No. | Spectral series | Lies in the region | Transition $n_2 > n_1$ | $\lambda_{\max} = \frac{n_1^2 n_2^2}{(n_2^2 - n_1^2)R}$ | $\lambda_{\min} = \frac{n_1^2}{R}$ | $\frac{\lambda_{\max}}{\lambda_{\min}} = \frac{n_2^2}{n_2^2 - n_1^2}$ |
|---|---|---|---|---|---|---|
| (1) | Lymen series | Ultraviolet region | $n_1 = 1$<br>$n_2 = 2,3,4....\infty$ | $n_1 = 1$ and $n_2 = 2$<br>$\lambda_{\max} = \frac{4}{3R}$ | $n_1 = 1$ and $n_2 = \infty$<br>$\lambda_{\min} = \frac{1}{R}$ | $\frac{4}{3}$ |
| (2) | Balmer series | Visible region | $n_1 = 2$<br>$n_2 = 3,4,5....\infty$ | $n_1 = 2$ and $n_2 = 3$<br>$\lambda_{\max} = \frac{36}{5R}$ | $n_1 = 2$ and $n_2 = \infty$<br>$\lambda_{\min} = \frac{4}{R}$ | $\frac{9}{5}$ |
| (3) | Paschen series | Infra red region | $n_1 = 3$<br>$n_2 = 4,5,6....\infty$ | $n_1 = 3$ and $n_2 = 4$<br>$\lambda_{\max} = \frac{144}{7R}$ | $n_1 = 3$ and $n_2 = \infty$<br>$\lambda_{\min} = \frac{9}{R}$ | $\frac{16}{7}$ |
| (4) | Brackett series | Infra red region | $n_1 = 4$<br>$n_2 = 5,6,7....\infty$ | $n_1 = 4$ and $n_2 = 5$<br>$\lambda_{\max} = \frac{16 \times 25}{9R}$ | $n_1 = 4$ and $n_2 = \infty$<br>$\lambda_{\min} = \frac{16}{R}$ | $\frac{25}{9}$ |
| (5) | Pfund series | Infra red region | $n_1 = 5$<br>$n_2 = 6,7,8....\infty$ | $n_1 = 5$ and $n_2 = 6$<br>$\lambda_{\max} = \frac{25 \times 36}{11R}$ | $n_1 = 5$ and $n_2 = \infty$<br>$\lambda_{\min} = \frac{25}{R}$ | $\frac{36}{11}$ |
| (6) | Humphrey series | Far infrared region | $n_1 = 6$<br>$n_2 = 7,8....\infty$ | $n_1 = 6$ and $n_2 = 7$<br>$\lambda_{\max} = \frac{36 \times 49}{13R}$ | $n_1 = 6$ and $n_2 = \infty$<br>$\lambda_{\min} = \frac{36}{R}$ | $\frac{49}{13}$ |

(v) If an electron from $n^{\text{th}}$ excited state comes to various energy states, the maximum spectral lines obtained will be = $\boxed{\frac{n(n-1)}{2}}$. $n$= principal quantum number.

as $n$=6 than total number of spectral lines = $\frac{6(6-1)}{2}=\frac{30}{2}=15$.

(vi) Thus, at least for the hydrogen atom, the Bohr Theory accurately describes the origin of atomic spectral lines.

(6) **Failure of Bohr Model**

(i) Bohr theory was very successful in predicting and accounting the energies of line spectra of hydrogen i.e. one electron system. It could not explain the line spectra of atoms containing more than one electron.

(ii) This theory could not explain the presence of multiple spectral lines.

(iii) This theory could not explain the splitting of spectral lines in magnetic field (Zeeman Effect) and in electric field (Stark effect). The intensity of these spectral lines was also not explained by the Bohr atomic model.

(iv) This theory was unable to explain of dual nature of matter as explained on the basis of De broglies concept.

(v) This theory could not explain uncertainty principle.

(vi) No conclusion was given for the concept of quantisation of energy.

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**Example: 18** If the radius of 2nd Bohr orbit of hydrogen atom is $r_2$. The radius of third Bohr orbit will be

(a) $\frac{4}{9}r_2$ (b) $4r_2$ (c) $\frac{9}{4}r_3$ (d) $9r_2$

**Solution : (c)** $r=\frac{n^2h^2}{4\pi^2 mZe^2}$ $\therefore$ $\frac{r_2}{r_3}=\frac{2^2}{3^2}$ $\therefore$ $r_3=\frac{9}{4}r_2$

**Example: 19** Number of waves made by a Bohr electron in one complete revolution in 3rd orbit is

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

**Solution : (b)** Circumference of 3rd orbit = $2\pi r_3$

According to Bohr angular momentum of electron in 3rd orbit is

$mvr_3 = 3\frac{h}{2\pi}$ or $\frac{h}{mv}=\frac{2\pi r_3}{3}$

by De-Broglie equation, $\lambda=\frac{h}{mv}$

$\therefore \lambda=\frac{2\pi r_3}{3}$ $\therefore 2\pi r_3=3\lambda$

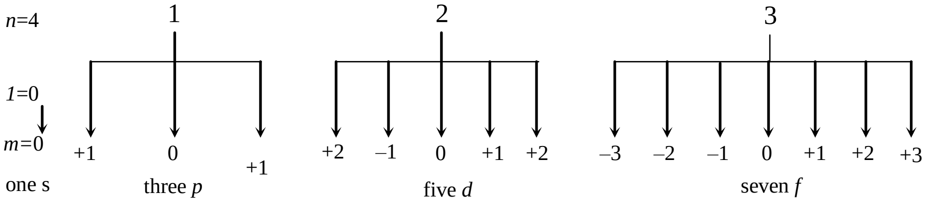
i.e. circumference of 3rd orbit is three times the wavelength of electron or number of waves made by Bohr electron in one complete revolution in 3rd orbit is three.

**Example: 20** The degeneracy of the level of hydrogen atom that has energy $-\frac{R_{11}}{16}$ is

(a) 16 (b) 4 (c) 2 (d) 1

**Solution : (a)** $E_n=-\frac{R_H}{n^2}$ $\therefore$ $-\frac{R_H}{n^2}=-\frac{R_H}{16}$

i.e. for $4^{th}$ sub-shell



i.e. 1+3+5+7=16, $\therefore$ degeneracy is 16

**Example: 21** The velocity of electron in the ground state hydrogen atom is $2.18\times10^{8}\,ms^{-1}$. Its velocity in the second orbit would be

(a) $1.09\times10^{8}\,ms^{-1}$ (b) $4.38\times10^{8}\,ms^{-1}$ (c) $5.5\times10^{5}\,ms^{-1}$ (d) $8.76\times10^{8}\,ms^{-1}$

**Solution : (a)** We know that velocity of electron in nth Bohr's orbit is given by

$$v = 2.18 \times 10^6 \frac{Z}{n} m/s$$

for $H, Z = 1$

$$\Theta \; v_1 = \frac{2.18 \times 10^6}{1} m/s$$

$$\Theta \; v_2 = \frac{2.18 \times 10^6}{2} m/s = 1.09 \times 10^6 m/s$$

**Example: 22** The ionization energy of the ground state hydrogen atom is $2.18 \times 10^{-18} J$. The energy of an electron in its second orbit would be

(a) $-1.09 \times 10^{-18} J$ (b) $-2.18 \times 10^{-18} J$ (c) $-4.36 \times 10^{-18} J$ (d) $-5.45 \times 10^{-19} J$

**Solution :** (d) Energy of electron in first Bohr's orbit of H-atom

$$E = \frac{-2.18 \times 10^{-18}}{n^2} J \quad (\Theta \text{ ionization energy of } H = 2.18 \times 10^{-18} J)$$

$$E_2 = \frac{-2.18 \times 10^{-18}}{2^2} J = -5.45 \times 10^{-19} J$$

**Example: 23** The wave number of first line of Balmer series of hydrogen atom is 15200 $cm^{-1}$. What is the wave number of first line of Balmer series of $Li^{3+}$ ion.

(a) 15200 $cm^{-1}$ (b) 6080 $cm^{-1}$ (c) 76000 $cm^{-1}$ (d) 1,36800 $cm^{-1}$

**Solution :** (d) For $Li^{3+}$ $\bar{v} = \bar{v}$ for $H \times z^2 = 15200 \times 9 = 1,36800\, cm^{-1}$

**Example: 24** The Bohr orbit radius for the hydrogen atom ($n$ = 1) is approximately 0.530Å. The radius for the first excited state ($n$ = 2) orbit is (in Å)

(a) 0.13 (b) 1.06 (c) 4.77 (d) 2.12

**Solution :** (d) The Bohr radius for hydrogen atom ($n$ = 1) = 0.530Å

The radius of first excited state ($n$ = 2) will be = $0.530 \times \frac{n^2}{Z} = 0.530 \times \frac{(2)^2}{1} = 2.120\, Å$

**Example: 25** How many chlorine atoms can you ionize in the process $Cl \rightarrow Cl^+ + e^-$, by the energy liberated from the following process :

$Cl + e^- \rightarrow Cl^-$ for $6 \times 10^{23}$ atoms

Given electron affinity of $Cl = 3.61 eV$, and $IP$ of $Cl = 17.422\, eV$

(a) $1.24 \times 10^{23}$ atoms (b) $9.82 \times 10^{20}$ atoms (c) $2.02 \times 10^{15}$ atoms (d) None of these

**Solution :** (a) Energy released in conversion of $6 \times 10^{23}$ atoms of $Cl^-$ ions = $6 \times 10^{23} \times$ electron affinity

$= 6 \times 10^{23} \times 3.61 = 2.166 \times 10^{24} eV.$

Let $x$ $Cl$ atoms are converted to $Cl^+$ ion

Energy absorbed $= x \times$ ionization energy

$x \times 17.422 = 2.166 \times 10^{24}$ ; $x = 1.243 \times 10^{23}$ atoms

**Example: 26** The binding energy of an electron in the ground state of the $He$ atom is equal to 24$eV$. The energy required to remove both the electrons from the atom will be

(a) 59$eV$ (b) 81$eV$ (c) 79$eV$ (d) None of these

**Solution :** (c) Ionization energy of $He$ $= \frac{Z^2}{n^2} \times 13.6 = \frac{2^2}{1^2} \times 13.6 = 54.4 eV$

Energy required to remove both the electrons

= binding energy + ionization energy

$= 24.6 + 54.4 = 79 eV$

**Example: 27** The wave number of the shortest wavelength transition in Balmer series of atomic hydrogen will be

(a) 4215 Å (b) 1437Å (c) 3942Å (d) 3647Å

**Solution :** (d) $\frac{1}{\lambda_{\text{shortest}}} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 109678 \times 1^2 \times \left(\frac{1}{2^2} - \frac{1}{\infty^2}\right)$

$\lambda = 3.647 \times 10^{-5} cm = 3647\, Å$

**Example: 28** If the speed of electron in the Bohr's first orbit of hydrogen atom is x, the speed of the electron in the third Bohr's orbit is

(a) $x/9$ (b) $x/3$ (c) $3x$ (d) $9x$

**Solution :** (b) According to Bohr's model for hydrogen and hydrogen like atoms the velocity of an electron in an atom is quantised and is given by $v \propto \frac{2\pi Ze^2}{nh}$ so $v \propto \frac{1}{n}$ in this cass $n = 3$

**Example: 29** Of the following transitions in hydrogen atom, the one which gives an absorption line of lowest frequency is

(a) $n=1$ to $n=2$ (b) $n = 3$ to $n = 8$ (c) $n = 2$ to $n = 1$ (d) $n = 8$ to $n = 3$

**Solution :** (b) Absorption line in the spectra arise when energy is absorbed i.e., electron shifts from lower to higher orbit, out of a & b, b will have the lowest frequency as this falls in the Paschen series.

**Example: 30** The frequency of the line in the emission spectrum of hydrogen when the atoms of the gas contain electrons in the third energy level are

(a) $1.268 \times 10^{14} Hz$ and $2.864 \times 10^{16} Hz$ (b) $3.214 \times 10^{10} Hz$ and $1.124 \times 10^{12} Hz$

(c) $1.806 \times 10^{12} Hz$ and $6.204 \times 10^{15} Hz$ (d) $4.568 \times 10^{14} Hz$ and $2.924 \times 10^{15} Hz$

**Solution :** (d) If an electron is in 3rd orbit, two spectral lines are possible

(a) When it falls from 3rd orbit to 2nd orbit.

In equation $v = 3.289 \times 10^{15}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$v_1 = 3.289 \times 10^{15}\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = 3.289 \times 10^{15} \times \frac{5}{36} = 4.568 \times 14^{14} Hz$$

(b) When it falls from 3rd orbit to 1st orbit :

$$v_2 = 3.289 \times 10^{15} \times \left[\frac{1}{1} - \frac{1}{3^2}\right] = 3.289 \times 10^{15} \times \frac{8}{9} = 2.924 \times 10^{15} Hz$$

**Example: 31** If the first ionisation energy of hydrogen is $2.179 \times 10^{-18} J$ per atom, the second ionisation energy of helium per atom is

(a) $8.716 \times 10^{-18} J$ (b) $5.5250 kJ$ (c) $7.616 \times 10^{-18} J$ (d) $8.016 \times 10^{-13} J$

**Solution :** (a) For Bohrs systems : energy of the electron $\propto \frac{Z^2}{n^2}$

Ionisation energy is the difference of energies of an electron $(E_\infty)$, when taken to infinite distance and $E_r$ when present in any Bohr orbit and $E_\alpha$ is taken as zero so ionisation energy becomes equal to the energy of electron in any Bohr orbit.

$E_H \propto \frac{Z_H^2}{n_H^2}$ ; $E_{He} \propto \frac{Z_{He}^2}{n_{He}^2}$ or $\frac{E_H}{E_{He}} = \frac{1}{2 \times 2}$ [as $Z_H = 1$, $Z_{He} = 2, n_H = 1, n_{He} = 1$]

or $E_{He} = E_H \times 4 = 2.179 \times 10^{-18} \times 4 = 8.716 \times 10^{-18}$ Joule per atom.

**Example: 32** The ionization energy of hydrogen atom is $13.6eV$. What will be the ionization energy of $He^+$

(a) 13.6eV (b) $54.4eV$ (c) $122.4eV$ (d) Zero

**Solution :** (b) I.E. of $He^+ = 13.6eV \times Z^2$

$13.6eV \times 4 = 54.4eV$

**Example: 33** The ionization energy of $He^+$ is $19.6 \times 10^{-18} J$ atom$^{-1}$. Calculate the energy of the first stationary state of $Li^{+2}$

(a) $19.6 \times 10^{-18} J$ atom $^{-1}$ (b) $4.41 \times 10^{-18} J$ atom$^{-1}$

(c) $19.6 \times 10^{-19} J$ atom $^{-1}$ (d) $4.41 \times 10^{-17} J$ atom $^{-1}$

**Solution :** (d) I.E. of $He^+ = E \times 2^2 (Z$ for $He = 2)$

I.E. of $Li^{2+} = E \times 3^3$ (Z for $Li$=3)

$\therefore \frac{I.E.(He^+)}{I.E.(Li^{2+})} = \frac{4}{9}$ or I.E. $(Li^{2+}) = \frac{9}{4} \times I.E.(He^+) = \frac{9}{4} \times 19.6 \times 10^{-18} = 4.41 \times 10^{-17}$ $J$ atom$^{-1}$

## Bohr – Sommerfeld's model

(1) In 1915, Sommerfield introduced a new atomic model to explain the fine spectrum of hydrogen atom.

(2) He gave concept that electron revolve round the nucleus in *elliptical orbit*. Circular orbits are formed in special conditions only when major axis and minor axis of orbit are equal.

(3) For circular orbit, the angular momentum = $\frac{nh}{2\pi}$ where $n$= principal quantum number only one component i.e. only angle changes.

(4) For elliptical orbit, angular momentum = vector sum of 2 components. In elliptical orbit two components are,

(i) Radial component (along the radius) $= n_r \dfrac{h}{2\pi}$

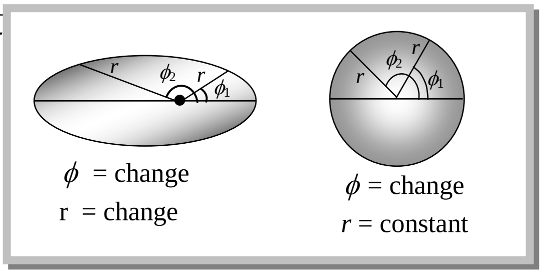
*Where,* $n_r$ = radial quantum number

(ii) Azimuthal component $= n_\phi \dfrac{h}{2\pi}$

*Where,* $n_\phi$ = azimuthal quantum number

So angular momentum of elliptical orbit $= n_r \dfrac{h}{2\pi} + n_\phi \dfrac{h}{2\pi}$

Angular momentum $= (n_r + n_\phi)\dfrac{h}{2\pi}$



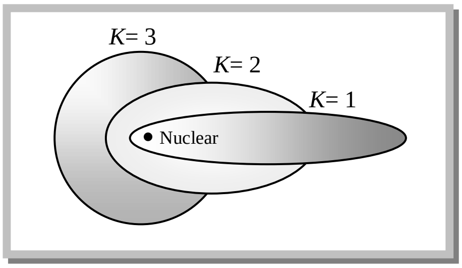
(5) Shape of elliptical orbit depends on,

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

(6) $n_\phi$ can take all integral values from $l$ to '$n$' values of $n_r$ depend on the value of $n_\phi$. For $n = 3$, $n_\phi$ can have values 1, 2, 3 and $n_r$ can have (n –1) to zero i.e. 2,1 and zero respectively.

Thus for n = 3, we have 3 paths

| $n$ | $n_\phi$ | $n_r$ | Nature of path |
|---|---|---|---|
| 3 | 1 | 3 | elliptical |
| | 2 | 1 | elliptical |
| | 3 | 0 | circular |



The possible orbits for n = 3 are shown in figure.

Thus *Sommerfield* showed that Bohr's each major level was composed of several sub-levels. therefore it provides the basis for existence of subshells in Bohr's shells (orbits).

(7) **Limitation of Bohr sommerfield model:**

(i) This model could not account for, why electrons does not absorb or emit energy when they are moving in stationary orbits.

(ii) When electron jumps from inner orbit to outer orbit or vice –versa, then electron run entire distance but absorption or emission of energy is discontinuous.

(iii) It could not explain the attainment of expression of $\dfrac{nh}{2\pi}$ for angular momentum. This model could not explain *Zeeman effect* and *Stark effect.*

---

## Dual nature of electron

(1) In 1924, the french physicist, ***Louis de Broglie*** suggested that if light has both particle and wave like nature, the similar duality must be true for matter. Thus an electron, behaves both as a material particle and as a wave.

(2) This presented a new wave mechanical theory of matter. According to this theory, small particles like electrons when in motion possess wave properties.

(3) According to de-broglie, the wavelength associated with a particle of mass $m$, moving with velocity $v$ is given by the relation

$\boxed{\lambda = \dfrac{h}{mv},}$ where $h$ = Planck's constant.

(4) This can be derived as follows according to Planck's equation, $E = h\nu = \dfrac{h.c}{\lambda} \quad \left(\Theta \;\; \nu = \dfrac{c}{\lambda}\right)$

energy of photon (on the basis of Einstein's mass energy relationship), $E = mc^2$

equating both $\dfrac{hc}{\lambda} = mc^2$ *or* $\lambda = \dfrac{h}{mc}$ which is same as de-Broglie relation. $(\Theta \;\; mc = p)$

(5) This was experimentally verified by ***Davisson and Germer*** by observing diffraction effects with an electron beam. Let the electron is accelerated with a potential of $V$ than the Kinetic energy is

$$\frac{1}{2}mv^2 = eV\ ;\quad m^2v^2 = 2eVm$$

$$mv = \sqrt{2eVm} = P\ ;\quad \lambda = \frac{h}{\sqrt{2eVm}}$$

(6) If Bohr's theory is associated with de-Broglie's equation then wave length of an electron can be determined in bohr's orbit and relate it with circumference and multiply with a whole number

$$2\pi r = n\lambda \text{ or } \lambda = \frac{2\pi r}{n}$$

From de-Broglie equation, $\lambda = \frac{h}{mv}$. Thus $\frac{h}{mv} = \frac{2\pi r}{n}$ or $mvr = \frac{nh}{2\pi}$

**Note :** ❑ For a proton, electron and an $\alpha$-particle moving with the same velocity have de-broglie wavelength in the following order : Electron > Proton > $\alpha$ - particle.

(7) The de-Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles. Since, we come across macroscopic objects in our everyday life, de-broglie relationship has no significance in everyday life.

---

**Example: 34** An electron is moving with a kinetic energy of $4.55 \times 10^{-25}$ $J$. What will be de-Broglie wavelength for this electron

(a) $5.28 \times 10^{-7}\ m$ (b) $7.28 \times 10^{-7} m$ (c) $2 \times 10^{-10} m$ (d) $3 \times 10^{-5} m$

**Solution :** (b) $KE = \frac{1}{2}mv^2 = 4.55 \times 10^{-25}\ J$

$$v^2 = \frac{2 \times 4.55 \times 10^{-25}}{9.1 \times 10^{-31}} = 1 \times 10^6\ ;\quad v = 10^3\ m/s$$

De-Broglie wavelength $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^3} = 7.28 \times 10^{-7}\ m$

**Example: 35** The speed of the proton is one hundredth of the speed of light in vacuum. What is the de Broglie wavelength? Assume that one mole of protons has a mass equal to one gram, $h = 6.626 \times 10^{-27}$ $erg$ sec

(a) $3.31 \times 10^{-3}$ Å (b) $1.33 \times 10^{-3}$ Å (c) $3.13 \times 10^{-2}$ Å (d) $1.31 \times 10^{-2}$ Å

**Solution :** (b) $m = \frac{1}{6.023 \times 10^{23}}\ g$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-27}}{1 \times 3 \times 10^8 cm\ \text{sec}^{-1}} \times 6.023 \times 10^{23} = 1.33 \times 10^{-11}\ cm$$

## Heisenberg's uncertainty principle

(1) One of the important consequences of the dual nature of an electron is the uncertainty principle, developed by ***Warner Heisenberg***.

(2) According to uncertainty principle "It is impossible to specify at any given moment both the position and momentum (velocity) of an electron".

Mathematically it is represented as , $\boxed{\Delta x . \Delta p \geq \frac{h}{4\pi}}$

Where $\Delta x =$ uncertainty is position of the particle, $\Delta p =$ uncertainty in the momentum of the particle

Now since $\Delta p = m\,\Delta v$

So equation becomes, $\Delta x . m\Delta v \geq \frac{h}{4\pi}$ or $\Delta x \times \Delta v \geq \frac{h}{4\pi m}$

The sign $\geq$ means that the product of $\Delta x$ and $\Delta p$ (or of $\Delta x$ and $\Delta v$) can be greater than, or equal to but never smaller than $\frac{h}{4\pi}$. If $\Delta x$ is made small, $\Delta p$ increases and vice versa.

(3) In terms of uncertainty in energy, $\Delta E$ and uncertainty in time $\Delta t,$ this principle is written as, $\Delta E.\Delta t \geq \frac{h}{4\pi}$

❑ Heisenberg's uncertainty principle cannot we apply to a stationary electron because its velocity is 0 and position can be measured accurately.

**Example: 36** What is the maximum precision with which the momentum of an electron can be known if the uncertainty in the position of electron is $\pm 0.001 \mathring{A}$? Will there be any problem in describing the momentum if it has a value of $\frac{h}{2\pi a_0}$, where $a_0$ is Bohr's radius of first orbit, i.e., 0.529Å?

**Solution :** $\Delta x.\Delta p = \frac{h}{4\pi}$

$\Theta\ \Delta x = 0.001\mathring{A} = 10^{-13} m$

$\therefore\ \Delta p = \frac{6.625\times 10^{-34}}{4\times 3.14\times 10^{-13}} = 5.27\times 10^{-22}$

**Example: 37** Calculate the uncertainty in velocity of an electron if the uncertainty in its position is of the order of a $1\mathring{A}$.

**Solution :** According to Heisenberg's uncertainty principle

$$\Delta v.\Delta x \approx \frac{h}{4\pi m}$$

$$\Delta v \approx \frac{h}{4\pi m.\Delta x} = \frac{6.625\times 10^{-34}}{4\times \frac{22}{7}\times 9.108\times 10^{-31}\times 10^{-10}} = 5.8\times 10^{5} m\ \sec^{-1}$$

**Example: 38** A dust particle having mass equal to $10^{-11} g,$ diameter of $10^{-4} cm$ and velocity $10^{-4} cm \sec^{-1}$. The error in measurement of velocity is 0.1%. Calculate uncertainty in its positions. Comment on the result .

**Solution :** $\Delta v = \frac{0.1\times 10^{-4}}{100} = 1\times 10^{-7} cm \sec^{-1}$

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

$\therefore\ \Delta x = \frac{6.625\times 10^{-27}}{4\times 3.14\times 10^{-11}\times 1\times 10^{-7}} = 5.27\times 10^{-10} cm$

The uncertainty in position as compared to particle size.

$= \frac{\Delta x}{diameter} = \frac{5.27\times 10^{-10}}{10^{-4}} = 5.27\times 10^{-6} cm$

The factor being small and almost being negligible for microscope particles.

---

## PLANCK'S QUANTUM THEORY

Q.11 Calculate the wavelength of the radiation that would cause photo dissociation of chlorine molecule if the Cl- Cl bond energy is 243 KJ/mol.

Q.12 Suppose $10^{-17}$ J of light energy is needed by the interior of the human eye to see an object. How many photons of green light ($\lambda$ = 550 nm) are needed to generate this minimum amount of energy.

Q.13 A photon having $\lambda$ = 854 Å causes the ionization of a nitrogen atom. Give the I.E. per mole of nitrogen in KJ.

Q.14 Calculate the threshold frequency of metal if the binding energy is 180.69 KJ $mol^{-1}$ of electron.

Q.15 Calculate the binding energy per mole when threshold frequency to the wavelength of 240 nm.

Q.16 A metal was irriadated by light of frequency $3.2 \times 10^{15}$ $S^{-1}$. The photoelectron produced had its KE, 2 times the KE of the photoelectron which was produced when the same metal was irriadated with a light of frequency $2.0 \times 10^{15}$ $S^{-1}$. What is work function.

Q.17 U.V. light of wavelength 800 Å & 700 Å falls on hydrogen atoms in their ground state & liberates electrons with kinetic energy 1.8 eV and 4 eV respectively. Calculate planck's constant.

Q.18 The dissociation energy of $H_2$ is 430.53 KJ/mol. If $H_2$ is exposed to radiant energy of wavelength 253.7 nm, what % of radiant energy will be converted into K.E.

Q.19 A potential difference of 20 KV is applied across an X-ray tube. Find the minimum wavelength of X-ray generated.

Q.20 The K.E. of an electron emitted from tungstan surface is 3.06 eV. What voltage would be required to bring the electron to rest?

## BOHR'S MODEL

Q.21 Calculate energy of electron which is moving in the orbit that has its rad. sixteen times the rad. of first Bohr orbit for H–atom.

Q.22 The electron energy in hydrogen atom is given by Calculate the energy required to remove an $e^-$ completely from n = 2 orbit . What is the largest wavelength in cm of light that can be used to cause this transition.

Q.23 Calculate the wavelength in angstrom of photon that is emitted when an $e^-$ in Bohr orbit n=2 returns to the orbit n=1. The ionization potential of the ground state of hydrogen atom is $2.17 \times 10^{-11}$ erg/atom.

Q.24 The radius of the fourth orbit of hydrogen atom is 0.85 nm. Calculate the velocity of electron in this orbit.

Q.25 The velocity of $e^-$ in a certain Bohr orbit of the hydrogen atom bears the ratio 1:275 to the velocity of light. What is the quantum no. "n" of the orbit and the wave no. of the radiation emitted for the transition from the quatum state (n+1) to the ground state.

Q.26 Electrons of energy 12.09 eV can excite hydrogen atoms. To which orbit is the electron in the hydrogen atom raised and what are the wavelengths of the radiations emitted as it drops back to the ground state.

Q.27 A doubly ionised lithium atom is hydrogen like with atomic number z = 3. Find the wavelength of the radiation required to excite the electron in $Li^{2+}$ from the first to the third Bohr orbit.

Q.28 Estimate the difference in energy between I and II Bohr Orbit for a hydrogen atom. At what minimum at no. a transition from n=2 to n=1 energy level would result in the emission of X–rays with $\lambda = 3.0 \times 10^{-8}$ m? Which hydrogen like species does this at no correspond to.

Q.29 Find out the no. of waves made by a Bohr electron in one complete revolution in its 3rd orbit.

Q.30 Iodine molecule dissociates into atoms after absorbing light of $4500A^0$. If one quantum of radiation is absorbed by each molecule, calculate the K.E. of iodine atoms
(Bond energy of $I_2$ = 240 KJ/mol)

Q.31 Calculate the wavelength of radiation emitted, producing a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom.

Q.32 Calculate the wave no. for the shortest wavelength transition in the Balmer series of atomic hydrogen.

## GENERAL

Q.33 What is de-Broglie wavelength of a He-atom in a container at room temperature.(Use $U_{avg}$)

Q.34 Through what potential difference must an electron pass to have a wavelength of 500 Å.

Q.35 A proton is accelerated to one- tenth of the velocity of light. If its velocity can be measured with a precision $\pm$ 1%. What must be its uncertainity in position.

Q.36 To what effective potential a proton beam be subjected to give its protons a wavelength of $1 \times 10^{-10}$ m.

Q.37 Calculate magnitude of angular momentum of an $e^-$ that occupies 1s, 2s , 2p , 3d , 3p.

Q.38 Calculate the number of exchange pairs of electrons present in configuration of Cu according to Aufbau Principle considering 3d & 4s orbitals.

Q.39 He atom can be excited to $1s^1\ 2p^1$ by $\lambda$ = 58.44 nm. If lowest excited state for He lies $4857\text{cm}^{-1}$ below the above. Calculate the energy for the lower excitation state.

Q.40 Wave functions of electrons in atoms & molecules are called________.

Q.41 The outermost electronic conf. of Cr is___________.

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## Answer Key

### PLANCK'S QUANTUM THEORY

Q.11 $4.9 \times 10^{-7}$ m Q.12 28 photons Q.13 1403 KJ/mol Q.14 $4.5 \times 10^{14}\ s^{-1}$
Q.15 497 KJ/mol Q.16 319.2 KJ/mol Q.17 $6.57 \times 10^{-34}$ Js
Q.18 8.68 % Q.19 0.62 Å Q.20 3.06 V

### *BOHR'S MODEL*

Q.21 $-1.36 \times 10^{-19}$ Joules Q.22 $-5.425\times10^{-12}$ ergs, $3.7\times10^{-5}$ cm
Q.23 1220 Å Q.24 $5.44 \times 10^{5}$ m/s Q.25 2 ; $9.75 \times 10^{4}\ \text{cm}^{-1}$
Q.26 3 , 6563 Å , 1215 Å , 1026 Å Q.27 113.74 Å
Q.28 10.2 eV , z = 2 Q.29 3 Q.30 $2.186 \times 10^{-20}$ Joules
Q.31 $9.7 \times 10^{-8}$ m Q.32 $27419.25\ \text{cm}^{-1}$

### *GENERAL*

Q.33 0.79 Å Q.34 $6.03\times10^{-4}$ volt Q.35 $1.05\times10^{-13}$ m
Q.36 0.0826 volts Q.37 0 ; 0 ; ; ; Q.38 25
Q.39 $3.3 \times 10^{-18}$ J Q.40 orbitals Q.41 $3s^2\ 3p^6\ 3d^5\ 4s^1$

## What is Wave Function?

In quantum physics, a wave function is a mathematical description of a quantum state of a particle as a function of momentum, time, position, and spin. The symbol used for a wave function is a Greek letter called psi, **Ψ**.

By using a wave function, the probability of finding an electron within the matter-wave can be explained. This can be obtained by including an imaginary number that is squared to get a real number solution resulting in the position of an electron. The concept of wave function was introduced in the year 1925 with the help of the Schrodinger equation.

## Properties of Wave Function

- All measurable information about the particle is available.
- **Ψ** should be continuous and single-valued.
- Using the Schrodinger equation, energy calculations becomes easy.
- Probability distribution in three dimensions is established using the wave function.
- The probability of finding a particle if it exists is 1.

### How is time independent Schrodinger equation represented?

The time independent Schrodinger equation represented as

$$[\frac{-h^2}{2m}\bigtriangledown^2 + V(r)]\Psi(r) = E\Psi(r)$$

### How is time-dependent Schrodinger equation represented?

The magnitude of the vector product is represented as:

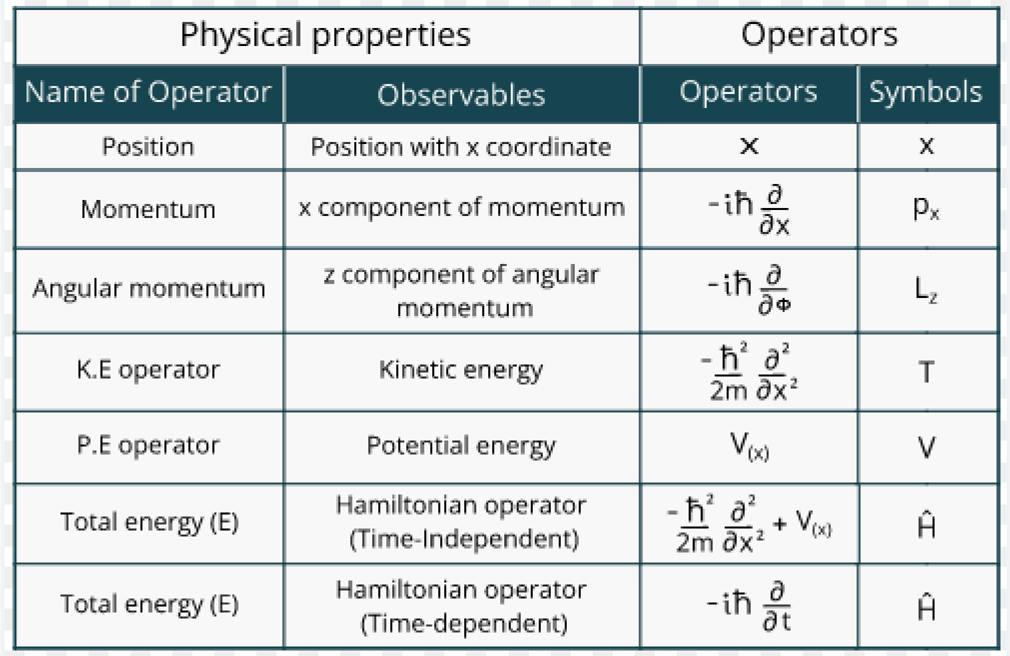
$$ih\frac{\partial}{\partial t}\Psi(r,t) = [\frac{h^2}{2m}\bigtriangledown^2 + V(r,t)]\Psi(r,t)$$

## Operator

An **operator** is a function over a space of physical states onto another space of physical states. Operators are important in quantum mechanics, where they form an intrinsic part of the formulation of the theory.

- **Workout: Example. Apply the following operators on the given functions:**
- **(a) Operator d/dx and function $x^2$.**
- **(b) Operator $d^2/dx^2$ and function $4x^2$.**
- **(c) Operator $(\partial/\partial y)x$ and function $xy^2$.**

- **(d) Operator $-i\hbar d/dx$ and function $\exp(-ikx)$.**
- **(e) Operator $-\hbar^2 d^2/dx^2$ and function $\exp(-ikx)$.**



| Physical properties | | Operators | |
|---|---|---|---|
| **Name of Operator** | **Observables** | **Operators** | **Symbols** |
| Position | Position with x coordinate | $x$ | $x$ |
| Momentum | x component of momentum | $-i\hbar\frac{\partial}{\partial x}$ | $p_x$ |
| Angular momentum | z component of angular momentum | $-i\hbar\frac{\partial}{\partial \Phi}$ | $L_z$ |
| K.E operator | Kinetic energy | $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ | T |
| P.E operator | Potential energy | $V_{(x)}$ | V |
| Total energy (E) | Hamiltonian operator (Time-Independent) | $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_{(x)}$ | $\hat{H}$ |
| Total energy (E) | Hamiltonian operator (Time-dependent) | $-i\hbar\frac{\partial}{\partial t}$ | $\hat{H}$ |

## Eigenvalues and Eigenfunctions

The wavefunction for a given physical system contains the measurable information about the system. To obtain specific values for physical parameters, for example energy, you operate on the wavefunction with the quantum mechanical operator associated with that parameter. The operator associated with energy is the Hamiltonian, and the operation on the wavefunction is the Schrodinger equation. Solutions exist for the time independent Schrodinger equation only for certain values of energy, and these values are called "eigenvalues*" of energy.

Corresponding to each eigenvalue is an "eigenfunction*".

$$Q_{op}\varphi_i = q_i\varphi_i$$

$Q_{op}$ = Operator

$\phi_i$ = Wavefunction

$q_i$ = Eigenvalue

if the function $\psi_i$ is an eigenfunction for that operator. The eigenvalues qi may be discrete, and in such cases we can say that the physical variable is "quantized" and that the index i plays the role of a "quantum number" which characterizes that state.

The solution to the Schrodinger equation for a given energy involves also finding the specific function which describes that energy state. The solution of the time independent Schrodinger equation takes the form

$$H_{op}\psi_i = E_i\psi_i$$

["Eigenvalue" comes from the German "Eigenwert" which means proper or characteristic value. "Eigenfunction" is from "Eigenfunktion" meaning "proper or characteristic function".]

**Ex:** $f(x) = e^{ikx}$ **Is it eigen function of momentum operator? What is eigenvalue?**

**Momentum operator is** $\hat{P}_x = -ih\frac{\partial}{\partial x}$

**ANS: Eigenvalue equation:**

(Operator) (function) = (constant factor)*(same function)

Or,

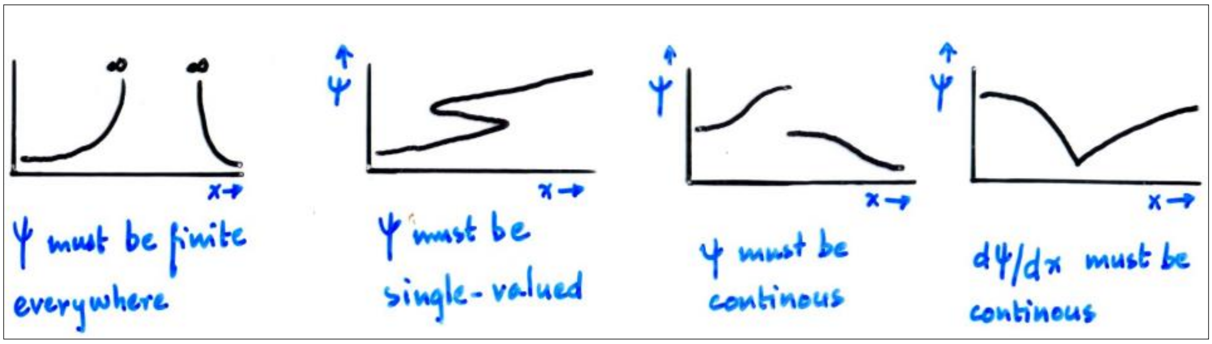
## How to check a function is quantum mechanically acceptable or not?

Condition for a physically accepted, well behaved, realistic wave function:

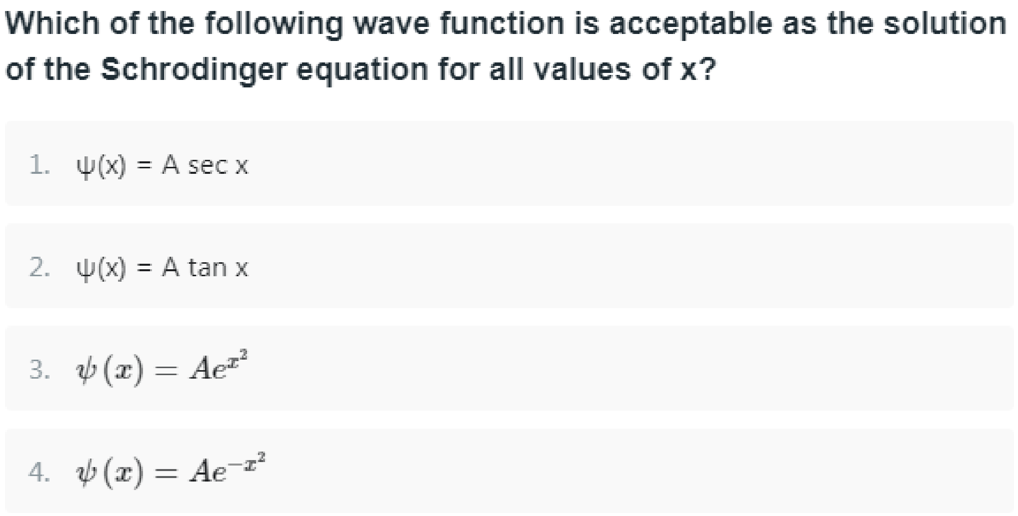
(i) ψ (x, t) should be finite, single-valued, and continuous everywhere in space.

(ii) dψ/dx should be continuous everywhere in space.

(iii) ψ(x, t) should be square-integrable.



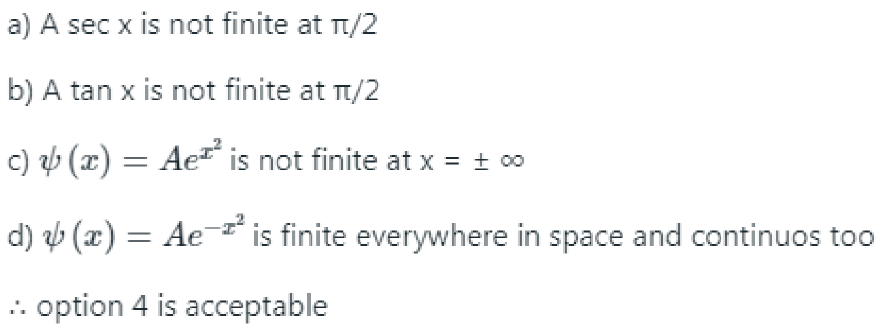
## Ex: 1



**Which of the following wave function is acceptable as the solution of the Schrodinger equation for all values of x?**

1. ψ(x) = A sec x
2. ψ(x) = A tan x
3. $\psi(x) = Ae^{x^2}$
4. $\psi(x) = Ae^{-x^2}$

## Ans:



a) A sec x is not finite at π/2

b) A tan x is not finite at π/2

c) $\psi(x) = Ae^{x^2}$ is not finite at x = ± ∞

d) $\psi(x) = Ae^{-x^2}$ is finite everywhere in space and continuos too

∴ option 4 is acceptable

## Ex: 2 Acceptable or not acceptable ??

$(i) e^{-x} (0, \infty)$

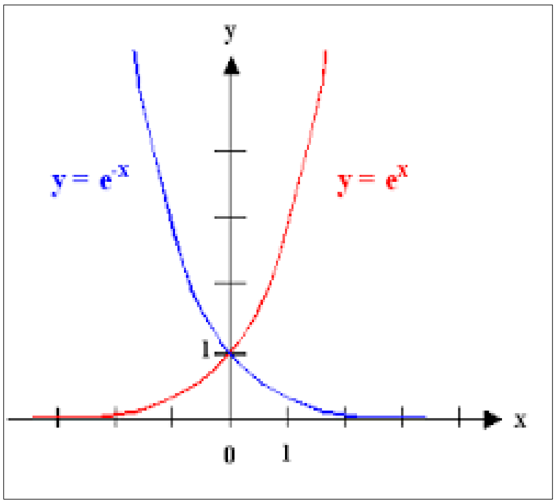
$(ii) e^{-x} (-\infty, \infty)$

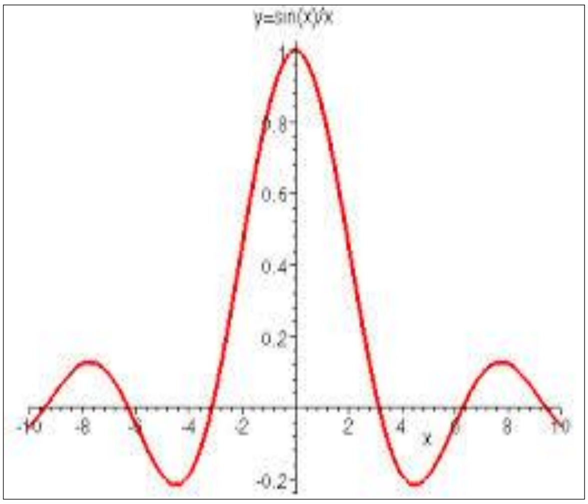
$(iii) \dfrac{\sin x}{x}$

$(iv) \sin^{-1} x$

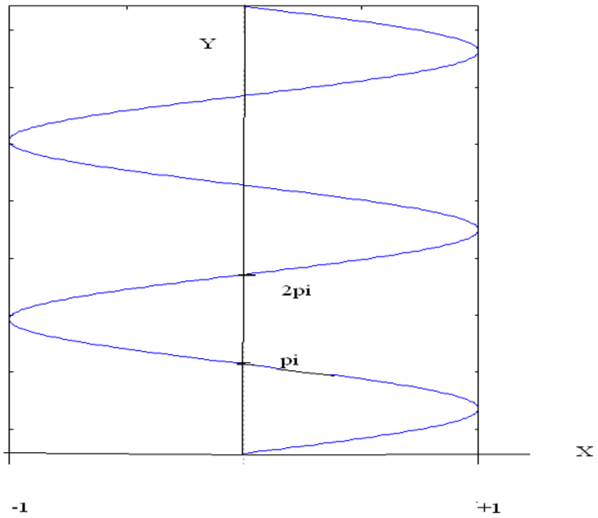
**Ans:**

**i) & iv) Exp(x)** **ii) Sinx/x**





**iii) $\mathbf{Sin^{-1}x}$**



y = arcsin(x)

## Solution of Schrodinger Equation:

In three dimensions the Schrodinger equation generalizes to,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi,$$

where $\Delta^2$ is the Laplacian operator. Using the Laplacian in spherical coordinates, the Schrodinger equation becomes

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi+V(r)\psi=E\psi.$$

In spherical coordinates, Ψ = Ψ(r, θ, ϕ), and the plan is to look for a variables separable solution such that Ψ(r, θ, ϕ = R(r) Y (θ,ϕ). We will in fact find such solutions where Y (θ,ϕ) are the spherical harmonic functions and R(r) is expressible in terms of associated Laguerre functions.

## Nature of different wave functions:

| $n$ | $l$ | $m$ | $\psi_{n,l,m}(r,\theta,\phi)$ |
|---|---|---|---|
| 1 | 0 | 0 | $\frac{1}{\sqrt{\pi}a_0^{3/2}}e^{-r/a_0}$ |
| 2 | 0 | 0 | $\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$ |
| 2 | 1 | 0 | $\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\cos\theta$ |
| 2 | 1 | $\pm1$ | $\frac{1}{8\sqrt{3\pi}a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\sin\theta\ e^{\pm i\phi}$ |
| 3 | 0 | 0 | $\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_o^2}\right)e^{-r/2a_o}$ |
| 3 | 1 | 0 | $\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\ \cos\theta$ |
| 3 | 1 | $\pm1$ | $\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\ \sin\theta\ e^{\pm i\phi}$ |
| 3 | 2 | 0 | $\frac{1}{81\sqrt{6\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ \left(3\cos^2\theta-1\right)$ |
| 3 | 2 | $\pm1$ | $\frac{1}{81\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ \sin\theta\cos\theta\ e^{\pm i\phi}$ |
| 3 | 2 | $\pm2$ | $\frac{1}{162\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ \sin^2\theta\ e^{\pm 2i\phi}$ |

**[Identify radial part and angular part in the above functions]**

Final solution of Schrodinger equation give 4 quantum numbers:

n = principal quantum number

l = Azimuthual quantum number

$m_l$ = Magnetic quantum number

$m_s$ = Spin quantum number

### Explanation for quantum number.

1. Quantum numbers are a collection of numbers that helps in describing the position as well as the energy of an electron.
2. There are 4 types of quantum numbers, that is, principal, azimuthal, magnetic, and spin quantum numbers.
3. An orbital is identified by 4 quantum numbers.
4. 4 quantum numbers are used to fully describe all of the attributes of a given electron.

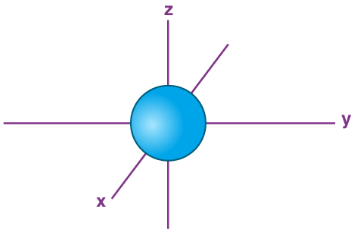
### Significance of quantum numbers.

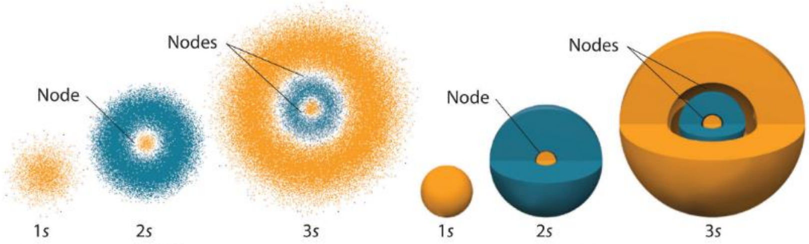
1. Principal quantum number: The size and energy of the orbit are defined by this quantum number.
2. Azimuthal quantum number: The shape of the orbitals is defined by this quantum number.
3. Magnetic quantum number: The spatial orientation of the orbital is determined by this quantum number.
4. Spin quantum number: The spin of the electron is indicated by this quantum number.

## The Shape of Orbitals:

**‘s’ Orbitals: Spherical Because its wave function has no angular dependence. By definition, an s orbital has zero angular momentum, and l=0. Any *nonzero* angular momentum leads to atomic orbitals having *non*-spherical shapes.**

- The boundary surface diagram for the s orbital looks like a sphere having the nucleus as its centre which in two dimensions can be seen as a circle.
- Hence, we can say that s-orbitals are spherically symmetric having the probability of finding the electron at a given distance equal in all the directions.
- The size of the s orbital is also found to increase with the increase in the value of the principal quantum number (n), thus, **4s > 3s> 2s > 1s**.



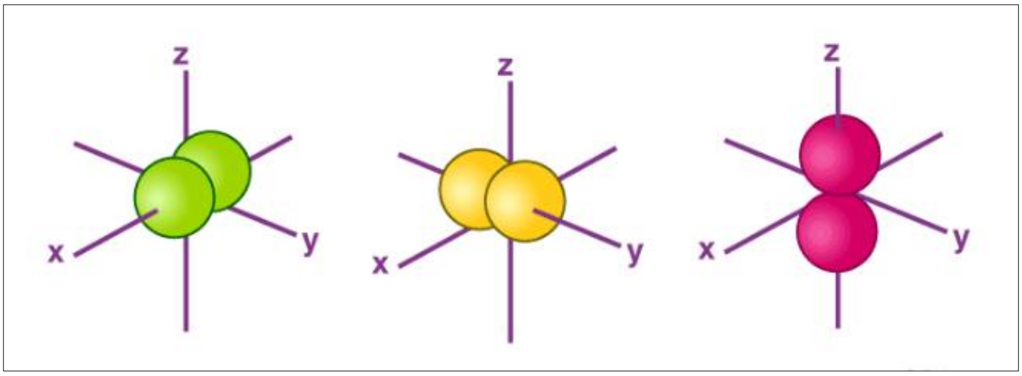


(a) Electron probability

(b) Contour probability

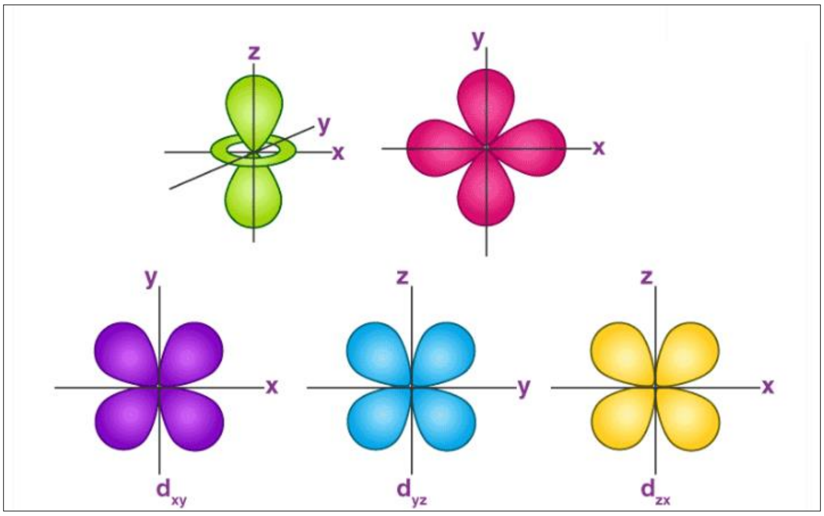
## The Shape of p Orbitals

- Each p orbital consists of two sections better known as lobes which lie on either side of the plane passing through the nucleus.
- The three p orbitals differ in the way the lobes are oriented whereas they are identical in terms of size, shape, and energy.
- As the lobes lie along one of the x, y or z-axis, these three orbitals are given the designations $2p_x$, $2p_y$, *and* $2p_z$. Thus, we can say that there are three p orbitals whose axes are mutually perpendicular.
- Similar to s orbitals the size, and energy of p orbitals increase with an increase in the principal quantum number (4p > 3p > 2p).



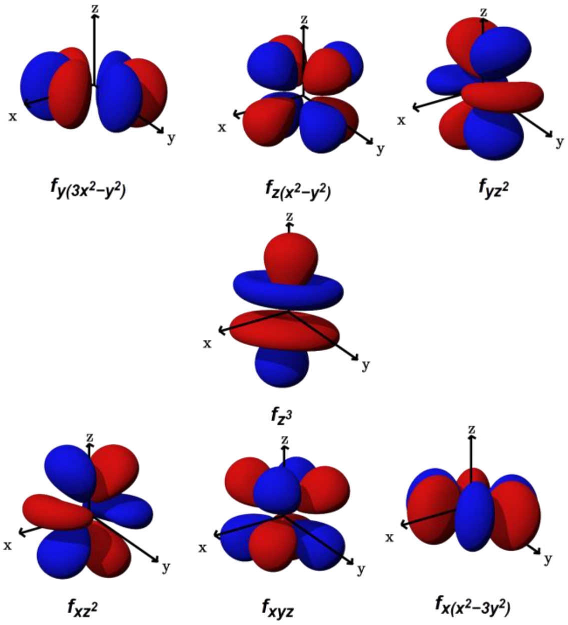
## The Shape of d Orbitals

- The magnetic orbital quantum number for d orbitals is given as (-2,-1,0, 1,2). Hence, we can say that there are five d-orbitals.
- These orbitals are designated as $d_{xy}$, $d_{yz}$, $d_{xz}$, $d_{x^2-y^2}$ and $d_{z^2}$.
- Out of these five *d* orbitals, the shapes of the first four *d*-orbitals are similar to each other, which is different from the $d_{z^2}$ orbital whereas the energy of all five d orbitals is the same



## The shape of the *f* orbital

The shape of the orbital is very complex. Though the shape is complex, the rule of filling of the electrons remains the same. The rule of alignment of the proton is the same as that of any *p* and *d* orbitals. When the *f* orbital gets completely filled, it just resembles the shape of the *d* orbital. But when it is cut into half, the f orbital divides into 8 lobes instead of the expected 4 lobes. This breaking of the lobes is based on the nucleus rotation, where the protons of opposite spin align on the points of the nucleus rotation.



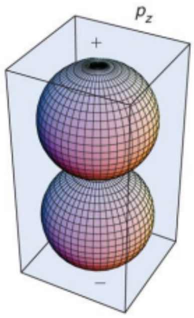
**Understanding shape of p orbitals: <u>For l = 1 and m = 0</u>, the angular function is,**

$$P_1^{|0|}(\cos\theta)=\sin^0\theta\left[\frac{d}{d(\cos\theta)}\right]^0\cos\theta=\cos\theta$$

$$Y_{1,0}(\theta,\phi)=\frac{1}{\sqrt{2\pi}}(-1)\sqrt{\frac{3}{2}}\cos(\theta)e^{i0\phi}=-\frac{\sqrt{3}}{2\sqrt{\pi}}\cos(\theta)$$

$$\left|Y_1^0\right|^2=const\times\cos^2\theta=\text{distance of surface from the origin}$$

| θ | $\cos^2\theta$ |
|---|---|
| 0 | 1 |
| 30 | 3/4 |
| 45 | 1/2 |
| 60 | 1/4 |
| 90 | 0 |

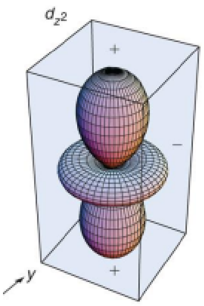


**Hence, the above function resulted in formation of $p_z$ orbital.**

**Similarly, for l =2 and m = 0,**

$$Y_{2,0}(\theta,\phi)=\frac{\sqrt{5}}{4\sqrt{\pi}}(3\cos^2(\theta)-1)$$

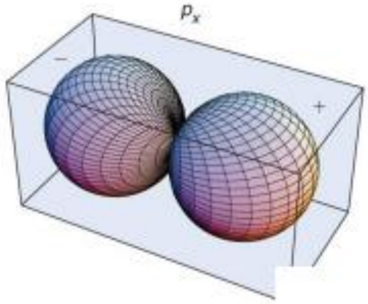
| θ | $\cos^2\theta$ | $3\cos^2\theta-1$ |
|---|---|---|
| 0 | 1 | 2 |
| 30 | 3/4 | (9/4-1)=5/4 |
| 45 | 1/2 | (3/2-1)=1/2 |
| 60 | 1/4 | (3/4-1)=-1/4 |
| 90 | 0 | -1 |



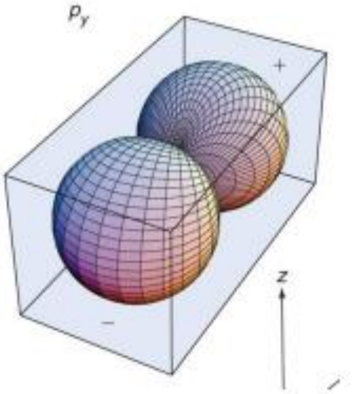
**For, l = 1, m = ±1**

$$\frac{1}{2}\left[Y_{1,+1}(\theta,\phi)+Y_{1,-1}(\theta,\phi)\right]=\mp\frac{\sqrt{3}}{4\sqrt{2\pi}}\sin(\theta)\left[e^{+i\phi}+e^{-i\phi}\right]=\mp\frac{\sqrt{3}}{2\sqrt{2\pi}}\sin(\theta)\cos(\phi)\in\square$$

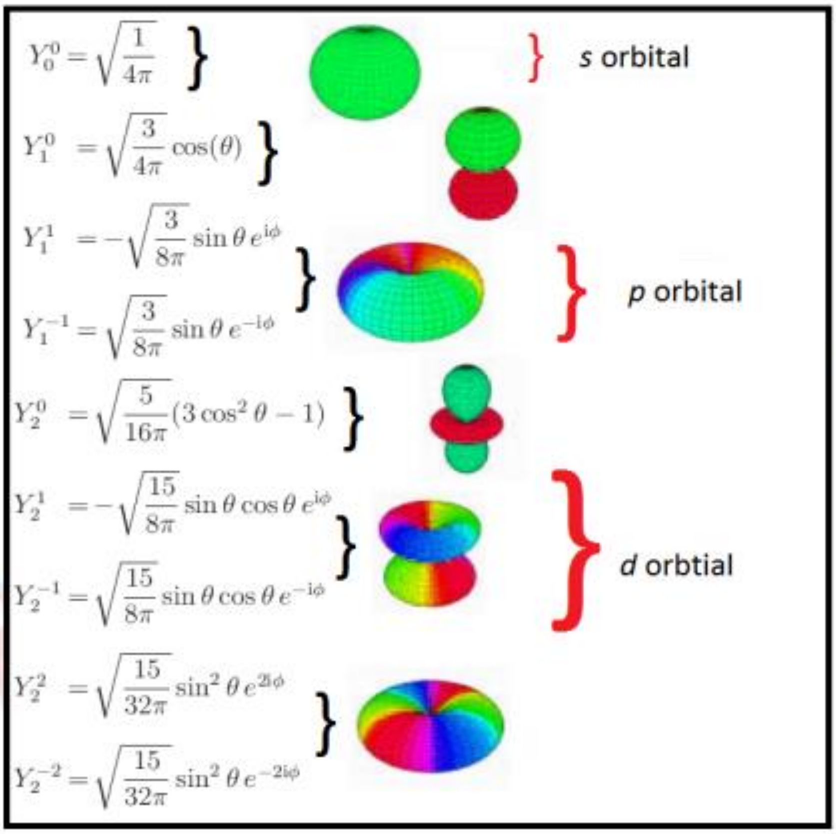
**Along x-axis**



$$\frac{1}{2i}\left[Y_{1,+1}(\theta,\phi)+Y_{1,-1}(\theta,\phi)\right]=\mp\frac{\sqrt{3}}{4i\sqrt{2\pi}}\sin(\theta)\left[e^{+i\phi}+e^{-i\phi}\right]=\mp\frac{\sqrt{3}}{2\sqrt{2\pi}}\sin(\theta)\sin(\phi)\in\square$$



## How azimuthal quantum number describe shape of the orbital! (only idea)



$$Y_0^0 = \sqrt{\frac{1}{4\pi}}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos(\theta)$$

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}$$

$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{i\phi}$$

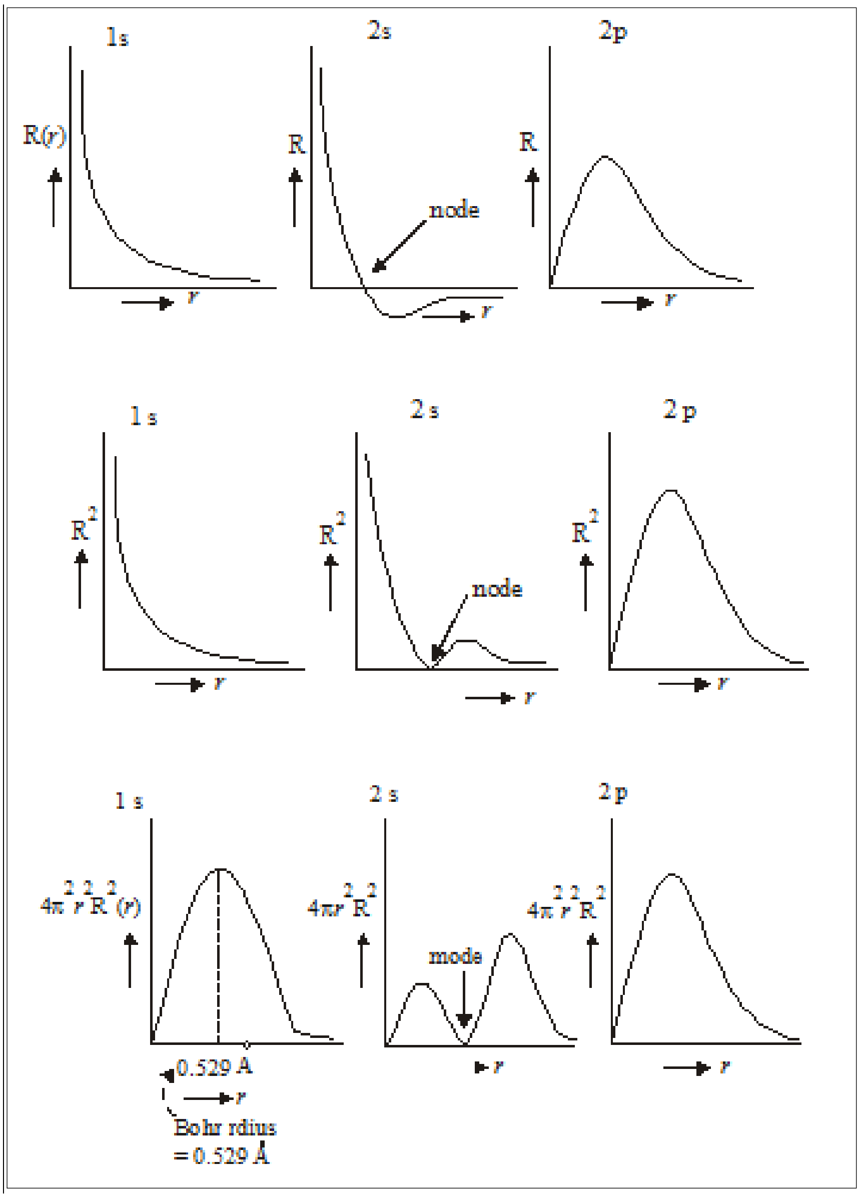
$$Y_2^{-1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{-i\phi}$$

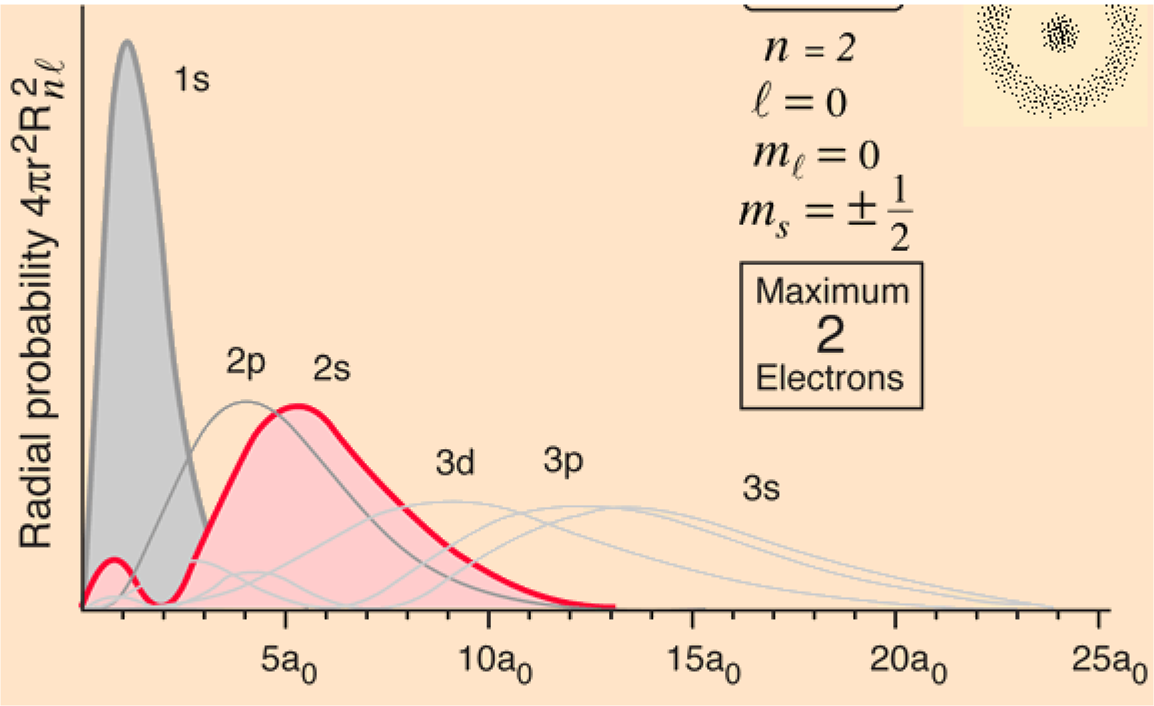
$$Y_2^2 = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\phi}$$

$$Y_2^{-2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{-2i\phi}$$

**Radial Probability Distribution Function:** The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the radial distribution function is given by $4\pi r^2(R(r))^2$.

## Graph:





## No. of nodes:

- Node is referred to as a point, where the probability of finding the electron is zero.
- There are two types of nodes, **angular node and radial node**

**Angular node**

- It is the plane that passes via the nucleus.
- An angular node is also known as a nodal plane.

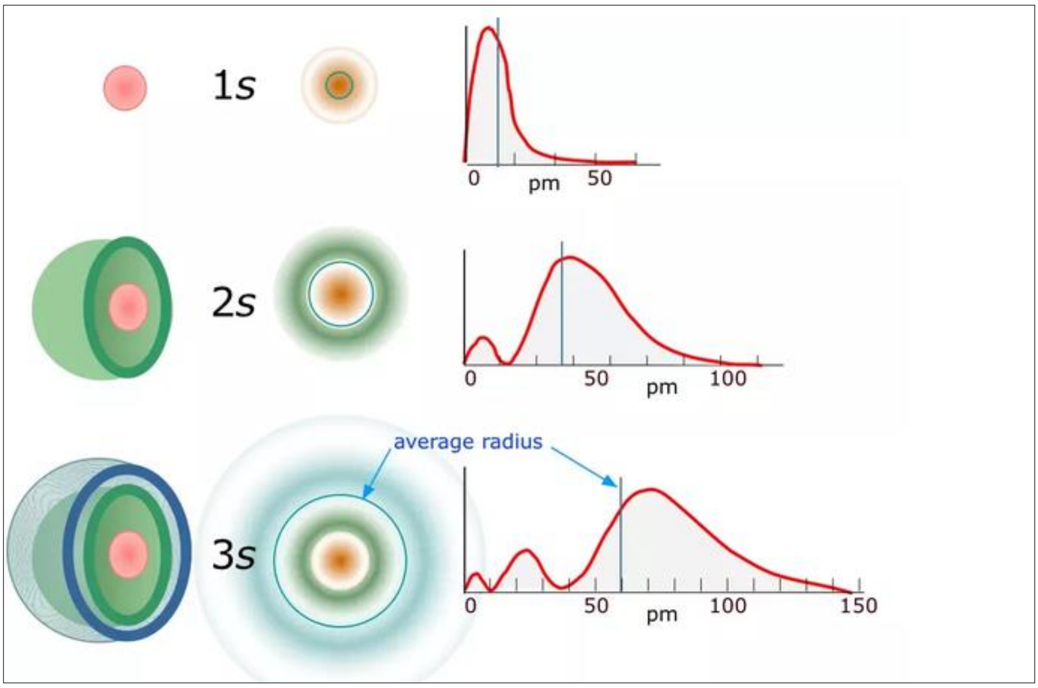
**Radial node**

- It is the spherical region where the probability of finding an electron is zero.
- The radial node is also known as the nodal region.

**Angular node = l**

**Radial node = n-l-1**

**Total nodes = radial nodes + angular nodes = n-1 where n is principal quantum number, l is azimuthal quantum number.**



## Electron Configuration

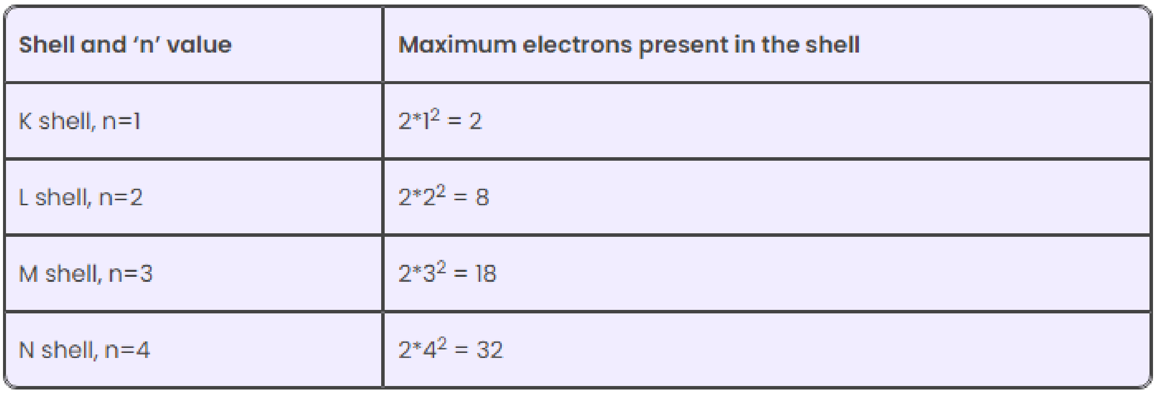
The electron configuration of an element describes how electrons are distributed in its atomic orbitals. Electron configurations of atoms follow a standard notation in which all electron-containing atomic subshells (with the number of electrons they hold written in superscript) are placed in a sequence. For example, the electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$.

Electron Configurations are useful for:

- Determining the valency of an element.
- Predicting the properties of a group of elements (elements with similar electron configurations tend to exhibit similar properties).
- Interpreting atomic spectra.

## Shells

The maximum number of electrons that can be accommodated in a shell is based on the principal quantum number (n). It is represented by the formula $2n^2$, where 'n' is the shell number. The shells, values of n, and the total number of electrons that can be accommodated are tabulated below.

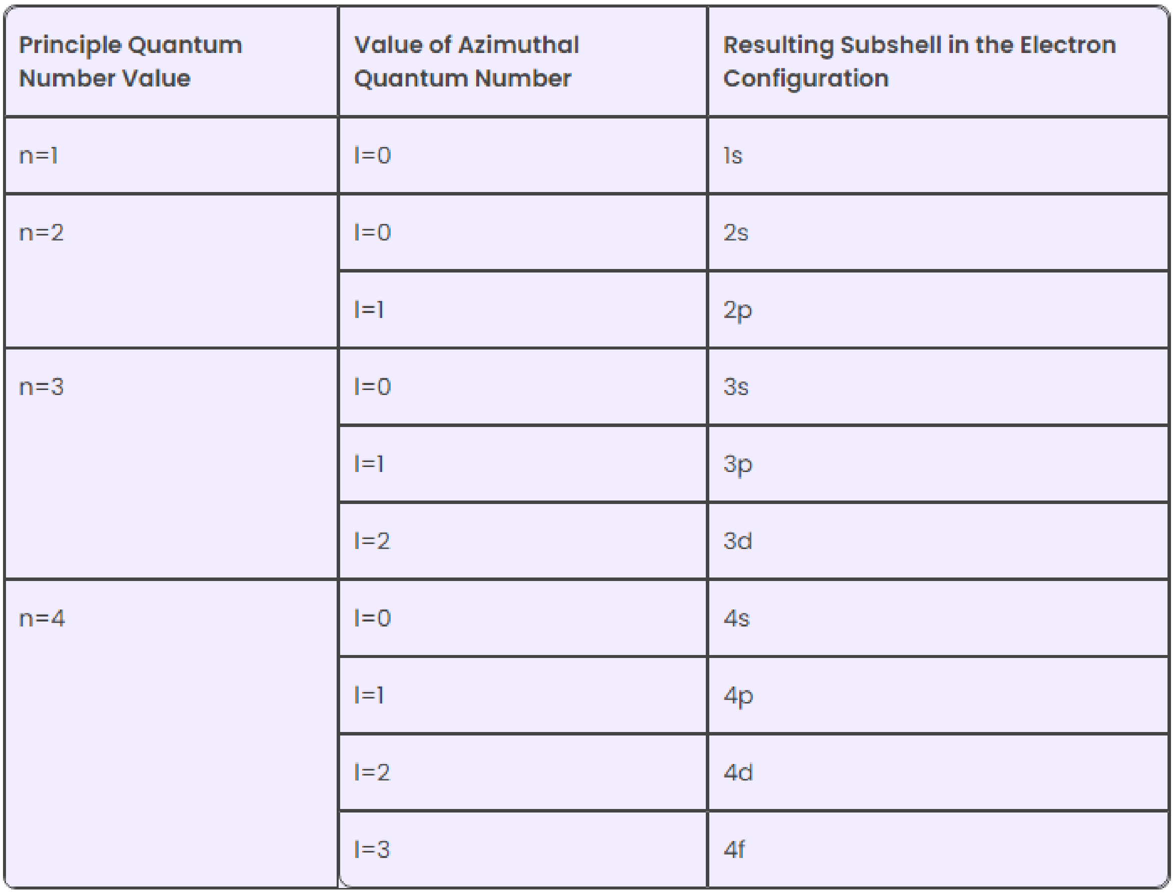


| Shell and 'n' value | Maximum electrons present in the shell |
|---|---|
| K shell, n=1 | $2*1^2 = 2$ |
| L shell, n=2 | $2*2^2 = 8$ |
| M shell, n=3 | $2*3^2 = 18$ |
| N shell, n=4 | $2*4^2 = 32$ |

## Subshells

- The subshells into which electrons are distributed are based on the azimuthal quantum number (denoted by 'l').
- This quantum number is dependent on the value of the principal quantum number, n. Therefore, when n has a value of 4, four different subshells are possible.
- When n=4. The subshells correspond to l=0, l=1, l=2, and l=3 and are named the s, p, d, and f subshells, respectively.
- The maximum number of electrons that can be accommodated by a subshell is given by the formula $2*(2l + 1)$.
- Therefore, the *s, p, d,* and *f* subshells can accommodate a maximum of 2, 6, 10, and 14 electrons, respectively.

All the possible subshells for values of n up to 4 are tabulated below



| Principle Quantum Number Value | Value of Azimuthal Quantum Number | Resulting Subshell in the Electron Configuration |
|---|---|---|
| n=1 | l=0 | 1s |
| n=2 | l=0 | 2s |
| | l=1 | 2p |
| n=3 | l=0 | 3s |
| | l=1 | 3p |
| | l=2 | 3d |
| n=4 | l=0 | 4s |
| | l=1 | 4p |
| | l=2 | 4d |
| | l=3 | 4f |

Thus, it can be understood that the 1p, 2d, and 3f orbitals do not exist because the value of the azimuthal quantum number is always less than that of the principal quantum number.

**Notation**

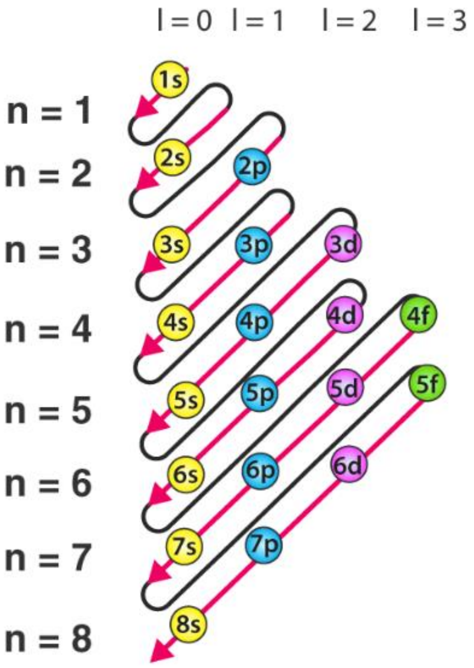
- The electron configuration of an atom is written with the help of subshell labels.
- These labels contain the shell number (given by the principal quantum number), the subshell name (given by the azimuthal quantum number) and the total number of electrons in the subshell in superscript.
- For example, if two electrons are filled in the ‘s’ subshell of the first shell, the resulting notation is ‘$1s^2$’.
- With the help of these subshell labels, the electron configuration of magnesium (atomic number 12) can be written as $1s^2\ 2s^2\ 2p^6\ 3s^2$.

## Filling of Atomic Orbitals

### Aufbau Principle

- This principle is named after the German word ‘Aufbeen’ which means ‘build up’.
- The Aufbau principle dictates that electrons will occupy the orbitals having lower energies before occupying higher energy orbitals.
- The energy of an orbital is calculated by the sum of the principal and the azimuthal quantum numbers.
- According to this principle, electrons are filled in the following order: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p…

The order in which electrons are filled in atomic orbitals as per the Aufbau principle is illustrated below.



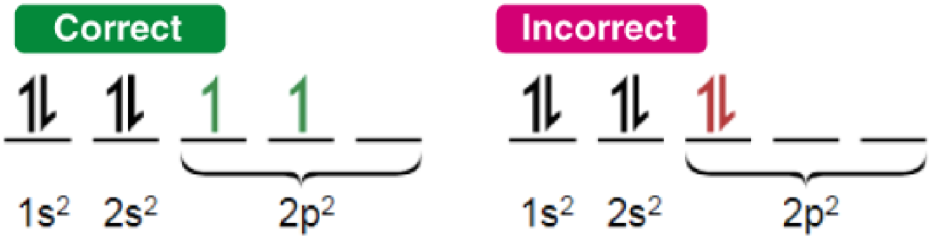
It is important to note that there exist many exceptions to the Aufbau principle such as chromium and copper. These exceptions can sometimes be explained by the stability provided by half-filled or completely filled subshells.

**Pauli Exclusion Principle**

- The Pauli exclusion principle states that a maximum of two electrons, each having opposite spins, can fit in an orbital.
- This principle can also be stated as “no two electrons in the same atom have the same values for all four quantum numbers”.
- Therefore, if the principal, azimuthal, and magnetic numbers are the same for two electrons, they must have opposite spins.

**Hund’s Rule**

- This rule describes the order in which electrons are filled in all the orbitals belonging to a subshell.
- It states that every orbital in a given subshell is singly occupied by electrons before a second electron is filled in an orbital.
- In order to maximize the total spin, the electrons in the orbitals that only contain one electron all have the same spin (or the same values of the spin quantum number).



An illustration detailing the manner in which electrons are filled in compliance with Hund’s rule of maximum multiplicity is provided above.

**<u>Representation of electronic Configuration of Atom</u>**

The electron configurations of a few elements are provided with illustrations in this subsection.

The electron configuration of chlorine is illustrated below. It can be written as **$1s^22s^22p^63s^23p^5$** or as $[Ne]3s^23p^5$

# Questions:

**1. Why is the s orbital spherical?**

**2. What does P orbital stand for?**

**3. What is sigma and pi bond?**

**4. Which orbitals have the highest energy?**

The orbital 1s hold the highest energy. You will appreciate it by talking of different things: But first let's be super clear: an electron's energy is the energy it will take to pull it out of the electrical bubble of the atom.

**5. What is the difference between a shell and an orbital?**

A shell in an atom is a set of subshells of the same quantum number theory, n. Orbitals contain two electrons each, and electrons are part of the same orbital in an orbital of the same definition of size, angular momentum size, and magnetic quantum number.

**6. What are the three rules that must be followed while writing the electronic configuration of elements?**

**7. What is the electronic configuration of copper?**

The electronic configuration of copper is [Ar]$3d^{10}4s^1$. This configuration disobeys the aufbau principle due to the relatively small energy gap between the 3d and the 4s orbitals. The completely filled d-orbital offers more stability than the partially filled configuration.

8. **Which of the following statements is/are correct?**

1) The radial probability distribution curves for 2s atomic orbital has one trough representing a radial node.

2) The radial probability distribution curves for 2s, 3p and 4d atomic orbitals are similar in shape (source: http://www.adichemistry.com)

3) The number of angular nodes cannot be found using radial distribution curves.

4) All

**Answer: 4**

**9. Which of the following atomic orbital with 1 angular node shows 3 maxima in its radial probability distribution curve?**

1) 3s

2) 5d

3) 4p

4) None of the above

**Answer: 3**

**10. The radial probability distribution curve obtained for an orbital wavefunction of valence electron of an alkaline earth metal atom has 4 peaks. The metal is:**

1) Potassium

2) Calcium

3) Barium

4) Magnesium

**Answer: 2**

**11. The number of peaks observed in the radial distribution curve for 4p atomic orbital is:**

A) 1

B) 2

C) 3

D) 0

**Answer: C**

**12. Is it possible to get the shapes of orbitals with the help of radial probability distribution curves?**

Answer: No. Since radial probability distribution curves are plotted for electron density at radial distance for a spherical shell, there is no direction or angle is mentioned. Hence it is not possible to get the exact shape of atomic orbitals from radial distribution curves. We have to take the support of angular distribution curves.

**13. What is exactly a radial node? (copied from adichemistry.com). What is the difference between an angular node and a radial node?**

Answer: Radial nodes are regions around the nucleus where the probability of finding electron is zero. They do not pass through the nucleus. The angular nodes are the planes where the probability of finding electron is zero and they pass through the nucleus.

**14. Calculate the number of radial nodes for 1s, 2s, 3s, 2p, 3p, 4p, 3d, 4d & 5d orbitals.**

Hint: Use the equation n-*l*-1.

**15. How many radial nodes are there in 4f orbital?**

Answer: number of radial nodes = n-*l*-1 = 4 - 3 - 1 = 0 radial nodes for 4f orbital.

**16. At what distance is the radial probability maximum for 1s orbital?**

**Answer: 0.053 nm. It is equal to the Bohr's radius of 1st orbit in hydrogen atom.**

**17. Radial probability distribution curves are the plots of $4\pi r^2\psi^2$ vs distance from the nucleus. The curve has number of maxima which is different for different orbitals. The number of spherical nodes present in 4p orbital and 5d orbital respectively are,................ (Answer: 2 & 2)**

**18. The variation of radial probability density $R^2$ (r) as a function of distance r of the electron from the nucleus for 3p orbital, when shown graphically, the graph shows .......... peaks with the smallest one ......... to the nucleus. (Answer: 2, closer)**

**19) The probability distribution curve for 2s electron appears like that of:**

1) 1s orbital

2) 2p orbital

3) 3p orbital

4) 3d orbital

**Answer: 3**

**10) Draw the graph of radius of orbit in hydrogen atom as a function of orbit number.**

**11) The radial probability curve obtained for an orbital wave function has 3 peaks and 2 radial nodes. The valence electron of which one of the following metals does this wave function correspond to:**

A) Ca

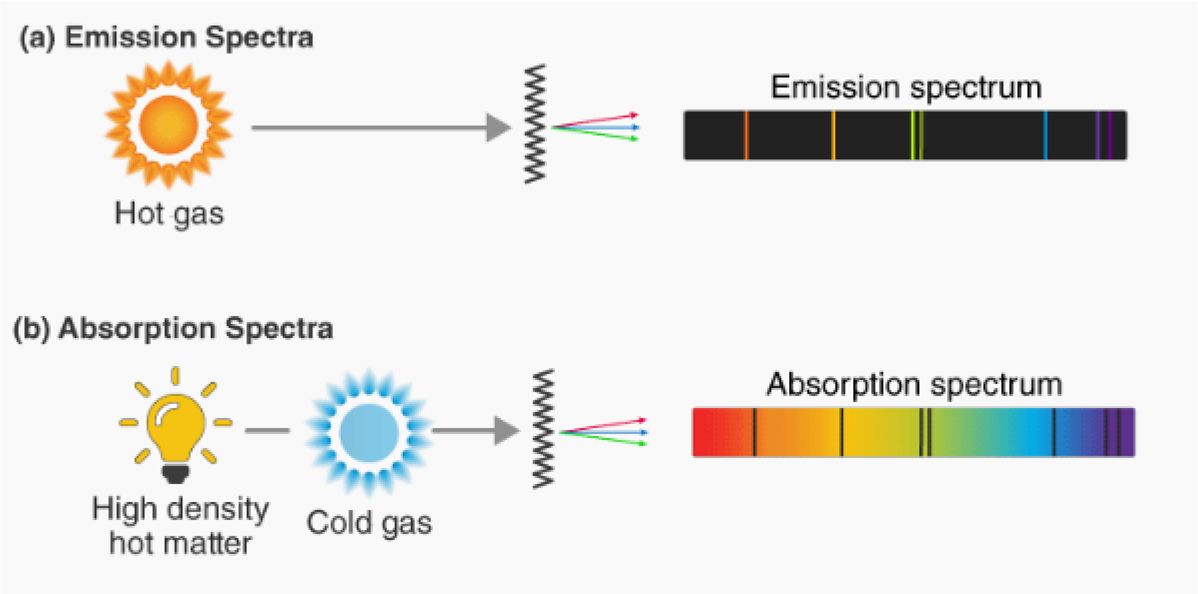
B) Mg

C) Li

D) Cs

**Answer: B**

**Emission spectra vs absorption spectra:**

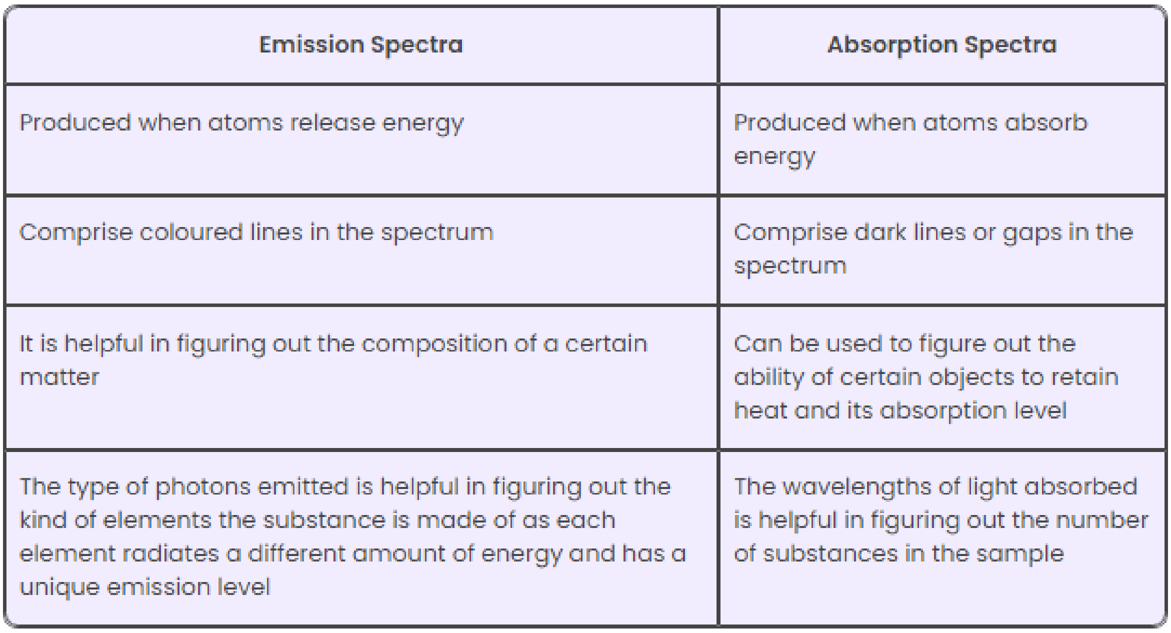


### What is an Emission Spectrum?

When energy is absorbed by electrons of an atom, electrons move from lower energy levels to higher energy levels. These excited electrons have to radiate energy to return to ground states from the excited state, which is unstable. The emission spectrum is formed by the frequencies of this emitted light.

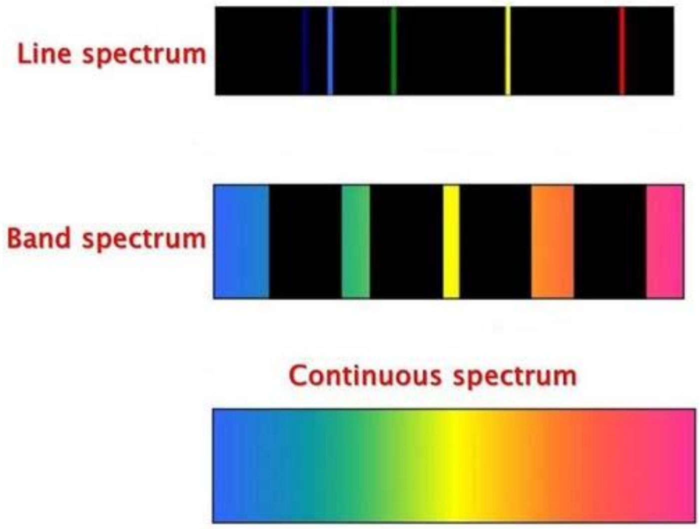
### What is the Absorption Spectrum?

On the other hand, an absorption spectrum is constituted by the frequencies of light transmitted with dark bands when energy is absorbed by the electrons in the ground state to reach higher energy states.



| Emission Spectra | Absorption Spectra |
|---|---|
| Produced when atoms release energy | Produced when atoms absorb energy |
| Comprise coloured lines in the spectrum | Comprise dark lines or gaps in the spectrum |
| It is helpful in figuring out the composition of a certain matter | Can be used to figure out the ability of certain objects to retain heat and its absorption level |
| The type of photons emitted is helpful in figuring out the kind of elements the substance is made of as each element radiates a different amount of energy and has a unique emission level | The wavelengths of light absorbed is helpful in figuring out the number of substances in the sample |

## Line spectrum and band spectrum:



A band spectrum is a molecular spectrum consisting of numerous closely spaced, often unresolved, emission lines or absorption lines which occur across a limited range of frequencies. Each line represents an increment of energy due to a change in the rotational state of a specific molecule.

The study of band spectra has played a crucial role in our understanding of the electronic structure of atoms and molecules, as well as in the development of technologies such as lasers and solar cells. At its most basic, a band spectrum arises when a substance absorbs or emits light at specific wavelengths or frequencies. These wavelengths or frequencies correspond to the energy levels that are present in the substance, and the intensity of the absorption or emission is proportional to the number of atoms or molecules that are present at each energy level.

The energy levels in a substance are typically organized into "bands," which are characterized by a range of energy levels that are closely spaced together.

There are two main types of band spectra: absorption spectra and emission spectra. An absorption spectrum is produced when a substance absorbs light, and is typically measured by shining light on the substance and measuring the amount of light that is absorbed at each wavelength or frequency. An emission spectrum, on the other hand, is produced when a substance emits light, and is typically measured by observing the light that is emitted by the substance when it is excited by an external energy source.

**Line spectrum:** When atoms are excited they emit light of certain wavelengths which correspond to different colors. The emitted light can be observed as a series of colored lines with dark spaces in between; this series of colored lines is called a line or atomic spectra. Each element produces a unique set of spectral lines. Since no two elements emit the same spectral lines, elements can be identified by their line spectrum.