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## Schrödinger wave equation

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- (1) Schrodinger wave equation is given by **Erwin Schrödinger** in 1926 and based on dual nature of electron.
- (2) In it electron is described as a three dimensional wave in the electric field of a positively charged nucleus.
- (3) The probability of finding an electron at any point around the nucleus can be determined by the help of Schrodinger wave equation which is,

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

Where  $x, y$  and  $z$  are the 3 space co-ordinates,  $m$  = mass of electron,  $h$  = Planck's constant,

$E$  = Total energy,  $V$  = potential energy of electron,  $\Psi$  = amplitude of wave also called as wave function.

$\partial$  = stands for an infinitesimal change.

- (4) The Schrodinger wave equation can also be written as :

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0$$

Where  $\nabla$  = laplacian operator.

- (5) **Physical Significance of  $\Psi$  and  $\Psi^2$**

- (i) The wave function  $\Psi$  represents the amplitude of the electron wave. The amplitude  $\Psi$  is thus a function of space co-ordinates and time i.e.  $\Psi = \Psi(x, y, z, \dots, t)$
- (ii) For a single particle, the square of the wave function ( $\Psi^2$ ) at any point is proportional to the probability of finding the particle at that point.
- (iii) If  $\Psi^2$  is maximum than probability of finding  $e^-$  is maximum around nucleus. And the place where probability of finding  $e^-$  is maximum is called *electron density*, electron cloud or an atomic orbital. It is different from the Bohr's orbit.
- (iv) The solution of this equation provides a set of number called *quantum numbers* which describe specific or definite energy state of the electron in atom and information about the shapes and orientations of the most probable distribution of electrons around the nucleus.

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## Quantum numbers and Shapes of orbitals

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### Quantum numbers

- (1) Each orbital in an atom is specified by a set of three quantum numbers ( $n, l, m$ ) and each electron is designated by a set of four quantum numbers ( $n, l, m$  and  $s$ ).

#### (2) Principle quantum number ( $n$ )

- (i) It was proposed by Bohr's and denoted by ' $n$ '.
- (ii) It determines the average distance between electron and nucleus, means it is denoted the size of atom.

$$r = \frac{n^2}{Z} \times 0.529 \text{ \AA}$$

- (iii) It determine the energy of the electron in an orbit where electron is present.

$$E = -\frac{Z^2}{n^2} \times 313.3 \text{ Kcal per mole}$$

- (iv) The maximum number of an electron in an orbit represented by this quantum number as  $2n^2$ . No energy shell in atoms of known elements possess more than 32 electrons.
- (v) It gives the information of orbit  $K, L, M, N, \dots$ .
- (vi) The value of energy increases with the increasing value of  $n$ .
- (vii) It represents the major energy shell or orbit to which the electron belongs.
- (viii) Angular momentum can also be calculated using principle quantum number

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

### (3) Azimuthal quantum number (*l*)

- (i) Azimuthal quantum number is also known as angular quantum number. Proposed by Sommerfeld and denoted by '*l*'.
- (ii) It determines the number of sub shells or sublevels to which the electron belongs.
- (iii) It tells about the shape of subshells.
- (iv) It also expresses the energies of subshells  $s < p < d < f$  (increasing energy).
- (v) The value of  $l = (n - 1)$  always where '*n*' is the number of principle shell.

|                        |   |           |          |                 |             |
|------------------------|---|-----------|----------|-----------------|-------------|
| (vi) Value of <i>l</i> | = | 0         | 1        | 2               | 3.....(n-1) |
| Name of subshell       | = | s         | p        | d               | f           |
| Shape of subshell      | = | Spherical | Dumbbell | Double dumbbell | Complex     |

- (vii) It represents the orbital angular momentum. Which is equal to?  $\frac{h}{2\pi} \sqrt{l(l+1)}$

- (viii) The maximum number of electrons in subshell  $= 2(2l + 1)$

*s* – subshell  $\rightarrow$  2 electrons   *d* – subshell  $\rightarrow$  10 electrons

*p* – subshell  $\rightarrow$  6 electrons   *f* – subshell  $\rightarrow$  14 electrons.

- (ix) For a given value of '*n*' the total value of '*l*' is always equal to the value of '*n*'.

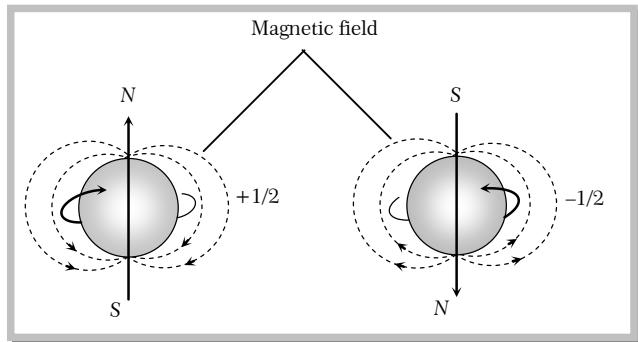
- (x) The energy of any electron is depend on the value of *n* & *l* because total energy  $= (n + l)$ . The electron enters in that sub orbit whose (*n* + *l*) value or the value of energy is less.

### (4) Magnetic quantum number (*m*)

- (i) It was proposed by Zeeman and denoted by '*m*'.
- (ii) It gives the number of permitted orientation of subshells.
- (iii) The value of *m* varies from  $-l$  to  $+l$  through zero.
- (iv) It tells about the splitting of spectral lines in the magnetic field i.e. this quantum number proved the Zeeman effect.
- (v) For a given value of '*n*' the total value of '*m*' is equal to  $n^2$ .
- (vi) For a given value of '*l*' the total value of '*m*' is equal to  $(2l + 1)$ .
- (vii) *Degenerate orbitals* : Orbitals having the same energy are known as degenerate orbitals. e.g. for *p* subshell *p<sub>x</sub>* *p<sub>y</sub>* *p<sub>z</sub>*
- (viii) The number of degenerate orbitals of *s* subshell  $= 0$ .

### (5) Spin quantum numbers (*s*)

- (i) It was proposed by Goldschmidt & Ulen Back and denoted by the symbol of '*s*'.
- (ii) The value of '*s*' is  $+1/2$  and  $-1/2$ , which signifies the spin or rotation or direction of electron on it's axis during movement.
- (iii) The spin may be clockwise or anticlockwise.
- (iv) It represents the value of spin angular momentum is equal to  $\frac{h}{2\pi} \sqrt{s(s+1)}$ .
- (v) Maximum spin of an atom  $= 1/2 \times$  number of unpaired electron.



- (vi) This quantum number is not the result of solution of Schrödinger equation as solved for  $H$ -atom.

## Distribution of electrons among the quantum levels

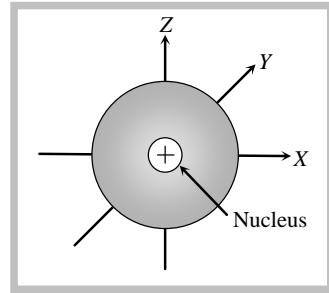
| <b>n</b>    | <b>l</b> | <b>m</b> | <b>s</b>   | Designation of orbitals | Electrons present | Total no. of electrons |
|-------------|----------|----------|------------|-------------------------|-------------------|------------------------|
| 1 (K shell) | 0        | 0        | +1/2, -1/2 | 1s                      | 2                 | 2                      |
| 2 (L shell) | 0        | 0        | +1/2, -1/2 | 2s                      | 2                 | 8                      |
|             |          | +1       | +1/2, -1/2 |                         |                   |                        |
|             | 1        | 0        | +1/2, -1/2 | 2p                      | 6                 |                        |
|             |          | -1       | +1/2, -1/2 |                         |                   |                        |
| 3 (M shell) | 0        | 0        | +1/2, -1/2 | 3s                      | 2                 | 18                     |
|             |          | +1       | +1/2, -1/2 |                         |                   |                        |
|             | 1        | 0        | +1/2, -1/2 | 3p                      | 6                 |                        |
|             |          | -1       | +1/2, -1/2 |                         |                   |                        |
|             |          |          | +1/2, -1/2 |                         |                   |                        |
|             |          | +2       | +1/2, -1/2 |                         |                   |                        |
|             |          | +1       | +1/2, -1/2 | 3d                      |                   |                        |
|             | 2        | 0        | +1/2, -1/2 |                         |                   |                        |
|             |          | -1       | +1/2, -1/2 |                         | 10                |                        |
|             |          | -2       |            |                         |                   |                        |
| 4(N shell)  | 0        | 0        | +1/2, -1/2 | 4s                      | 2                 | 32                     |
|             |          | +1       | +1/2, -1/2 |                         |                   |                        |
|             | 1        | 0        | +1/2, -1/2 | 4p                      | 6                 |                        |
|             |          | -1       | +1/2, -1/2 |                         |                   |                        |
|             |          |          | +1/2, -1/2 |                         |                   |                        |
|             |          | +2       | +1/2, -1/2 |                         |                   |                        |
|             |          | +1       | +1/2, -1/2 | 4d                      |                   |                        |
|             | 2        | 0        | +1/2, -1/2 |                         |                   |                        |
|             |          | -1       | +1/2, -1/2 |                         | 10                |                        |
|             |          | -2       | +1/2, -1/2 |                         |                   |                        |
|             |          |          |            |                         |                   |                        |
|             |          | +3       |            |                         |                   |                        |
|             |          | +2       |            |                         |                   |                        |
|             |          | +1       |            |                         |                   |                        |
|             | 3        | +0       |            | 4f                      |                   |                        |
|             |          | -1       |            |                         | 14                |                        |

|  |  |    |                 |  |  |  |
|--|--|----|-----------------|--|--|--|
|  |  | -2 | + 1 / 2, -1 / 2 |  |  |  |
|  |  | -3 | + 1 / 2, -1 / 2 |  |  |  |
|  |  |    | + 1 / 2, -1 / 2 |  |  |  |
|  |  |    | + 1 / 2, -1 / 2 |  |  |  |
|  |  |    | + 1 / 2, -1 / 2 |  |  |  |
|  |  |    | + 1 / 2, -1 / 2 |  |  |  |
|  |  |    | + 1 / 2, -1 / 2 |  |  |  |

## Shape of orbitals

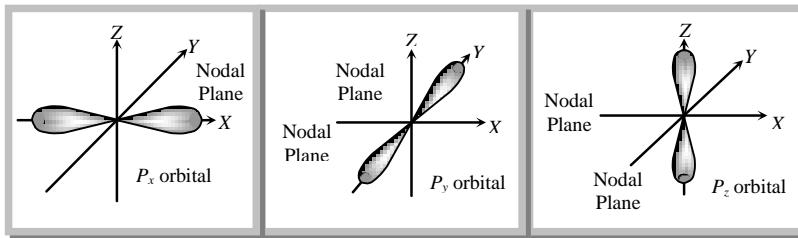
### (1) Shape of 's' orbital

- (i) For 's' orbital  $l=0$  &  $m=0$  so 's' orbital have only one unidirectional orientation i.e. the probability of finding the electrons is same in all directions.
- (ii) The size and energy of 's' orbital with increasing 'n' will be  $1s < 2s < 3s < 4s$ .
- (iii) It does not possess any directional property. s orbital has spherical shape.



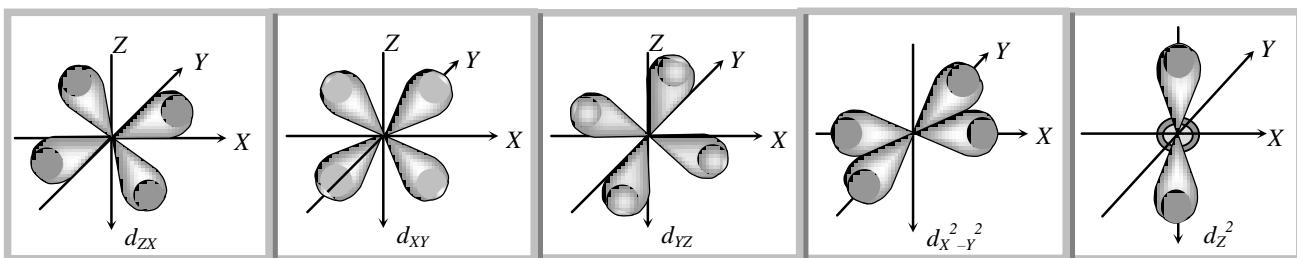
### (2) Shape of 'p' orbitals

- (i) For 'p' orbital  $l=1$ , &  $m=+1, 0, -1$  means there are three 'p' orbitals, which is symbolised as  $p_x, p_y, p_z$ .
- (ii) Shape of 'p' orbital is dumb bell in which the two lobes on opposite side separated by the nodal plane.
- (iii)  $p$ -orbital has directional properties.



### (3) Shape of 'd' orbital

- (i) For the 'd' orbital  $l=2$  then the values of 'm' are  $-2, -1, 0, +1, +2$ . It shows that the 'd' orbitals has five orbitals as  $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$ .
- (ii) Each 'd' orbital identical in shape, size and energy.
- (iii) The shape of d orbital is double dumb bell .
- (iv) It has directional properties.



#### (4) Shape of 'f' orbital

- (i) For the 'f' orbital  $l=3$  then the values of 'm' are  $-3, -2, -1, 0, +1, +2, +3$ . It shows that the 'f' orbitals have seven orientation as  $f_{x(x^2-y^2)}$ ,  $f_{y(x^2-y^2)}$ ,  $f_{z(x^2-y^2)}$ ,  $f_{xyz}$ ,  $f_z^3$ ,  $f_{yz}^3$  and  $f_{xz}^3$ .
- (ii) The 'f' orbital is complicated in shape.

### **Electronic configuration principles**

The distribution of electrons in different orbitals of atom is known as electronic configuration of the atoms.

Filling up of orbitals in the ground state of atom is governed by the following rules:

#### (1) Aufbau principle

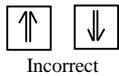
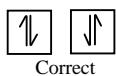
- (i) Aufbau is a German word, meaning 'building up'.
- (ii) According to this principle, "In the ground state, the atomic orbitals are filled in order of increasing energies i.e. in the ground state the electrons first occupy the lowest energy orbitals available".
- (iii) In fact the energy of an orbital is determined by the quantum number  $n$  and  $l$  with the help of  $(n+l)$  rule or Bohr Bury rule.
- (iv) According to this rule
  - (a) Lower the value of  $n + l$ , lower is the energy of the orbital and such an orbital will be filled up first.
  - (b) When two orbitals have same value of  $(n+l)$  the orbital having lower value of " $n$ " has lower energy and such an orbital will be filled up first .

Thus, order of filling up of orbitals is as follows:

$$1s < 2s < 2p < 3s < 3p < 4s < 4p < 5s < 4d < 5p < 6s < 6f < 5d$$

#### (2) Pauli's exclusion principle

- (i) According to this principle, "No two electrons in an atom can have same set of all the four quantum numbers  $n, l, m$  and  $s$  .
- (ii) In an atom any two electrons may have three quantum numbers identical but fourth quantum number must be different.
- (iii) Since this principle excludes certain possible combinations of quantum numbers for any two electrons in an atom, it was given the name exclusion principle. Its results are as follows :
  - (a) The maximum capacity of a main energy shell is equal to  $2n^2$  electron.
  - (b) The maximum capacity of a subshell is equal to  $2(2l+1)$  electron.
  - (c) Number of sub-shells in a main energy shell is equal to the value of  $n$ .
  - (d) Number of orbitals in a main energy shell is equal to  $n^2$ .
  - (e) One orbital cannot have more than two electrons.
- (iv) According to this principle an orbital can accommodate at the most two electrons with spins opposite to each other. It means that an orbital can have 0, 1, or 2 electron.
- (v) If an orbital has two electrons they must be of opposite spin.



### (3) Hund's Rule of maximum multiplicity

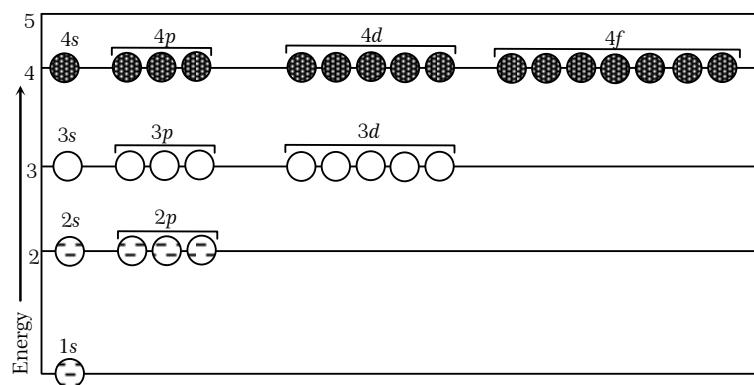
- (i) This rule provides the basis for filling up of degenerate orbitals of the same sub-shell.
- (ii) According to this rule "Electron filling will not take place in orbitals of same energy until all the available orbitals of a given subshell contain one electron each with parallel spin".
- (iii) This implies that electron pairing begins with fourth, sixth and eighth electron in  $p$ ,  $d$  and  $f$  orbitals of the same subshell respectively.
- (iv) The reason behind this rule is related to repulsion between identical charged electron present in the same orbital.
- (v) They can minimise the repulsive force between them by occupying different orbitals.
- (vi) Moreover, according to this principle, the electron entering the different orbitals of subshell have parallel spins. This keeps them farther apart and lowers the energy through electron exchange or resonance.
- (vii) The term maximum multiplicity means that the total spin of unpaired  $e^-$  is maximum in case of correct filling of orbitals as per this rule.

#### *Energy level diagram*

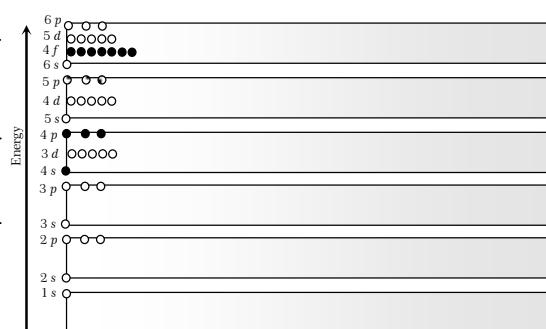
The representation of relative energy levels of various atomic orbital is made in the terms of energy level diagrams.

**One electron system:** In this system  $1s^2$  level and all orbital of same principal quantum number have same energy, which is independent of ( $l$ ). In this system  $l$  only determines the shape of the orbital.

**Multiple electron system:** The energy levels of such system not only depend upon the nuclear charge but also upon the another electron present in them.



*Energy level diagram of one electron system*



*Energy level diagram of multiple electron system*

Diagram of multi-electron atoms reveals the following points :

- (i) As the distance of the shell increases from the nucleus, the energy level increases. For example energy level of  $2 > 1$ .
- (ii) The different sub shells have different energy levels which possess definite energy. For a definite shell, the subshell having higher value of  $l$  possesses higher energy level. For example in  $4^{\text{th}}$  shell.

Energy level order     $4f > 4d > 4p > 4s$   
                              $l=3 \quad l=2 \quad l=1 \quad l=0$

(iii) The relative energy of sub shells of different energy shell can be explained in the terms of the  $(n+l)$  rule.

(a) The sub-shell with lower values of  $(n + l)$  possesses lower energy.

For     $3d \quad n = 3 \quad l = 2 \quad \therefore n + l = 5$

For     $4s \quad n = 4 \quad l = 0 \quad n + l = 4$

(b) If the value of  $(n + l)$  for two orbitals is same, one with lower values of 'n' possess lower energy level.

### Extra stability of half filled and completely filled orbitals

Half-filled and completely filled sub-shell have extra stability due to the following reasons :

#### (i) Symmetry of orbitals

(a) It is a well known fact that symmetry leads to stability.

(b) Thus, if the shift of an electron from one orbital to another orbital differing slightly in energy results in the symmetrical electronic configuration. It becomes more stable.

(c) For example  $p^3, d^5, f^7$  configurations are more stable than their near ones.

#### (ii) Exchange energy

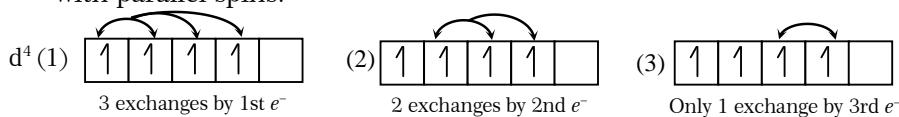
(a) The electron in various subshells can exchange their positions, since electron in the same subshell have equal energies.

(b) The energy is released during the exchange process with in the same subshell.

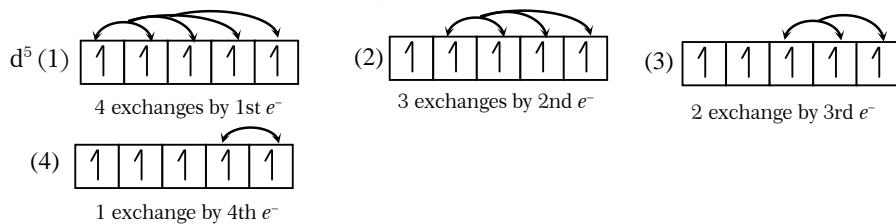
(c) In case of half filled and completely filled orbitals, the exchange energy is maximum and is greater than the loss of orbital energy due to the transfer of electron from a higher to a lower sublevel e.g. from  $4s$  to  $3d$  orbitals in case of  $Cu$  and  $Cr$ .

(d) The greater the number of possible exchanges between the electrons of parallel spins present in the degenerate orbitals, the higher would be the amount of energy released and more will be the stability.

(e) Let us count the number of exchange that are possible in  $d^4$  and  $d^5$  configuraton among electrons with parallel spins.



To number of possible exchanges =  $3 + 2 + 1 = 6$



To number of possible exchanges =  $4 + 3 + 2 + 1 = 10$

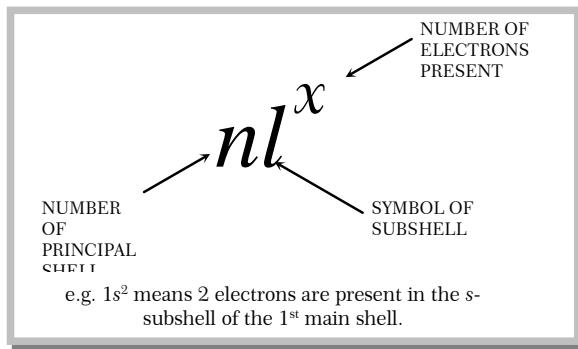
## Electronic configurations of Elements

(1) On the basis of the electronic configuration principles the electronic configuration of various elements are given in the following table :

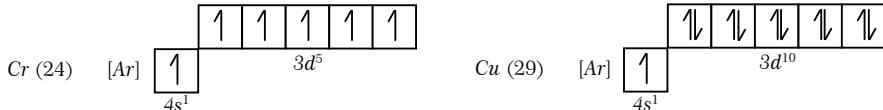
**Electronic Configuration (E.C.) of Elements Z=1 to 36**

| Element | Atomic Number | 1s        | 2s | 2p | 3s | 3p | 3d | 4s | 4p | 4d | 4f |
|---------|---------------|-----------|----|----|----|----|----|----|----|----|----|
| H       | 1             | 1         |    |    |    |    |    |    |    |    |    |
| He      | 2             | 2         |    |    |    |    |    |    |    |    |    |
| Li      | 3             | 2         | 1  |    |    |    |    |    |    |    |    |
| Be      | 4             | 2         | 2  |    |    |    |    |    |    |    |    |
| B       | 5             | 2         | 2  | 1  |    |    |    |    |    |    |    |
| C       | 6             | 2         | 2  | 2  |    |    |    |    |    |    |    |
| N       | 7             | 2         | 2  | 3  |    |    |    |    |    |    |    |
| O       | 8             | 2         | 2  | 4  |    |    |    |    |    |    |    |
| F       | 9             | 2         | 2  | 5  |    |    |    |    |    |    |    |
| Ne      | 10            | 2         | 2  | 6  |    |    |    |    |    |    |    |
| Na      | 11            | 2         | 2  | 6  | 1  |    |    |    |    |    |    |
| Mg      | 12            |           |    |    | 2  |    |    |    |    |    |    |
| Al      | 13            |           |    |    | 2  | 1  |    |    |    |    |    |
| Si      | 14            | 10        |    |    | 2  | 2  |    |    |    |    |    |
| P       | 15            | electrons |    |    | 2  | 3  |    |    |    |    |    |
| S       | 16            |           |    |    | 2  | 4  |    |    |    |    |    |
| Cl      | 17            |           |    |    | 2  | 5  |    |    |    |    |    |
| Ar      | 18            | 2         | 2  | 6  | 2  | 6  |    |    |    |    |    |
| K       | 19            | 2         | 2  | 6  | 2  | 6  |    | 1  |    |    |    |
| Ca      | 20            |           |    |    |    |    |    | 2  |    |    |    |
| Sc      | 21            |           |    |    |    |    | 1  | 2  |    |    |    |
| Ti      | 22            |           |    |    |    |    | 2  | 2  |    |    |    |
| V       | 23            |           |    |    |    |    | 3  | 2  |    |    |    |
| Cr      | 24            |           |    |    |    |    | 5  | 1  |    |    |    |
| Mn      | 25            |           |    |    |    |    | 5  | 2  |    |    |    |
| Fe      | 26            |           |    |    |    |    | 6  | 2  |    |    |    |
| Co      | 27            | 18        |    |    |    |    | 7  | 2  |    |    |    |
| Ni      | 28            | electrons |    |    |    |    | 8  | 2  |    |    |    |
| Cu      | 29            |           |    |    |    |    | 10 | 1  |    |    |    |
| Zn      | 30            |           |    |    |    |    | 10 | 2  |    |    |    |
| Ga      | 31            |           |    |    |    |    | 10 | 2  | 1  |    |    |
| Ge      | 32            |           |    |    |    |    | 10 | 2  | 2  |    |    |
| As      | 33            |           |    |    |    |    | 10 | 2  | 3  |    |    |
| Se      | 34            |           |    |    |    |    | 10 | 2  | 4  |    |    |
| Br      | 35            |           |    |    |    |    | 10 | 2  | 5  |    |    |
| Kr      | 36            | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  |    |    |

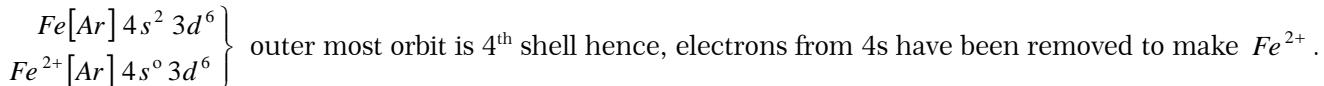
(2) The above method of writing the electronic configurations is quite cumbersome. Hence, usually the electronic configuration of the atom of any element is simply represented by the notation.



- (3) (i) Elements with atomic number 24(Cr), 42(Mo) and 74(W) have  $ns^1(n-1)d^5$  configuration and not  $ns^2(n-1)d^4$  due to extra stability of these atoms.
- (ii) Elements with atomic number 29(Cu), 47(Ag) and 79(Au) have  $ns^1(n-1)d^{10}$  configuration instead of  $ns^2(n-1)d^9$  due to extra stability of these atoms.



- (4) In the formation of ion, electrons of the outer most orbit are lost. Hence, whenever you are required to write electronic configuration of the ion, first write electronic configuration of its atom and take electron from outermost orbit. If we write electronic configuration of  $Fe^{2+}$  ( $Z = 26, 24 e^-$ ), it will not be similar to Cr (with  $24 e^-$ ) but quite different.



- (5) Ion/atom will be paramagnetic if there are unpaired electrons. Magnetic moment (spin only) is  $\mu = \sqrt{n(n+2)}$  BM (Bohr Magneton). ( $1BM = 9.27 \times 10^{-24} J/T$ ) where  $n$  is the number of unpaired electrons.

- (6) Ion with unpaired electron in  $d$  or  $f$  orbital will be coloured. Thus,  $Cu^+$  with electronic configuration  $[Ar]3d^{10}$  is colourless and  $Cu^{2+}$  with electronic configuration  $[Ar]3d^9$  (one unpaired electron in 3d) is coloured (blue).

- (7) Position of the element in periodic table on the basis of electronic configuration can be determined as,

- (i) If last electron enters into s-subshell, p-subshell, penultimate d-subshell and anti penultimate f-subshell then the element belongs to s, p, d and f-block respectively.
- (ii) Principle quantum number ( $n$ ) of outermost shell gives the number of period of the element.
- (iii) If the last shell contains 1 or 2 electrons (i.e. for s-block elements having the configuration  $ns^{1-2}$ ), the group number is 1 in the first case and 2 in the second case.
- (iv) If the last shell contains 3 or more than 3 electrons (i.e. for p-block elements having the configuration  $ns^2 np^{1-6}$ ), the group number is the total number of electrons in the last shell plus 10.
- (v) If the electrons are present in the  $(n-1)d$  orbital in addition to those in the  $ns$  orbital (i.e. for d-block elements having the configuration  $(n-1)d^{1-10} ns^{1-2}$ ), the group number is equal to the total number of electrons present in the  $(n-1)d$  orbital and  $ns$  orbital.

## **EXERCISE**

- Q.1** X-rays emitted from a copper target and a molybdenum target are found to contain a line of wavelength 22.85 nm attributed to the  $K_{\alpha}$  line of an impurity element. The  $K_{\alpha}$  lines of copper ( $Z = 29$ ) and molybdenum ( $Z = 42$ ) have wavelength 15.42 nm and 7.12 nm respectively. Using Moseley's law,  $\gamma^{1/2} = a(Z - b)$  calculate the atomic number of the impurity element.
- Q.2** Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral lines of lowest energy in the visible region of its atomic spectra.
- Q.3** 1.8 g hydrogen atoms are excited to radiations. The study of spectra indicates that 27% of the atoms are in 3rd energy level and 15% of atoms in 2nd energy level and the rest in ground state. If I.P. of H is  $21.7 \times 10^{-12}$  erg. Calculate –  
(i) No. of atoms present in III & II energy level.  
(ii) Total energy evolved when all the atoms return to ground state.
- Q.4** One mole  $He^+$  ions are excited. Spectral analysis showed existence of 50% ions in 3<sup>rd</sup> orbit, 25% in 2<sup>nd</sup> and rest in ground state. Calculate total energy evolved when all the ions return to the ground state.
- Q.5** The energy of an excited H-atom is  $-3.4$  eV. Calculate angular momentum of  $e^-$ .
- Q.6** The vapours of Hg absorb some electrons accelerated by a potential diff. of 4.5 volt as a result of which light is emitted. If the full energy of single incident  $e^-$  is supposed to be converted into light emitted by single Hg atom, find the wave no. of the light.
- Q.7** The hydrogen atom in the ground state is excited by means of monochromatic radiation of wavelength  $x A^0$ . The resulting spectrum consists of 15 different lines . Calculate the value of x.
- Q.8** The eyes of certain member of the reptile family pass a single visual signal to the brain when the visual receptors are struck by photons of wavelength 850 nm . If a total energy of  $3.15 \times 10^{-14}$  J is required to trip the signal, what is the minimum number of photons that must strike the receptor.
- Q.9** If the average life time of an excited state of H atom is of order  $10^{-8}$  sec, estimate how many orbits an  $e^-$  makes when it is in the state  $n = 2$  and before it suffers a transition to  $n = 1$  state.
- Q.10** Calculate the frequency of  $e^-$  in the first Bohr orbit in a H-atom.
- Q.11** A single electron orbits around a stationary nucleus o f charge  $+Ze$  where Z is a constant from the nucleus and e is the magnitude of the electric charge. The hydrogen like species required 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Find  
(i) the value of Z and give the hydrogen like species formed.  
(ii) the kinetic energy and potential energy of the electron in the first Bohr orbit.
- Q.12** A stationary  $He^+$  ion emitted a photon corresponding to a first line of the Lyman series. The photon liberated a photon electron from a stationary H atom in ground state. What is the velocity of photoelectron.
- Q.13** To what series does the spectral lines of atomic hydrogen belong if its wave number is equal to the difference between the wave numbers of the following two lines of the Balmer series 486.1 and 410.2 nm. What is the wavelength of this.
- Q.14** A particle of charge equal to that of an electron and mass 208 times the mass of the electron moves in a circular orbit around a nucleus of charge  $+3e$ . Assuming that the Bohr model of the atom is applicable to this system, (a) derive an expression for the radius of the nth bohr orbit, (b) find the value of n for which the radius of the orbit is approximately the same as that of the first Bohr orbit for the hydrogen atom, and (c) find the wavelength of the radiation emitted when the revolving particle jumps from the third orbit to the first.

- Q.15 The ionisation energy of the hydrogen atom is given to be 13.6 eV. A photon falls on a hydrogen atom which is initially in the ground state and excites it to the ( $n = 4$ ) state.
- (a) show this transition in the energy-level diagram &  
 (b) calculate the wavelength of the photon.
- Q.16 Find the number of photons of radiation of frequency  $5 \times 10^{13} \text{ s}^{-1}$  that must be absorbed in order to melt one gm ice when the latent heat of fusion of ice is 330 J/g.
- Q.17 The dye acriflavine, when dissolved in water, has its maximum light absorption at  $4530 \text{ \AA}$  and its maximum fluorescence emission at  $5080 \text{ \AA}$ . The number of fluorescence quanta is, on the average, 53% of the number of quanta absorbed. Using the wavelengths of maximum absorption and emission, what % of absorbed energy is emitted as fluorescence?
- Q.18 Hydrogen atom in its ground state is excited by means of monochromatic radiation of wavelength  $975 \text{ \AA}$ . How many different lines are possible in the resulting spectrum? Calculate the longest wavelength amongst them.
- Q.19 An alpha particle after passing through a potential difference of  $2 \times 10^6$  volt falls on a silver foil. The atomic number of silver is 47. Calculate (i) the K.E. of the alpha-particle at the time of falling on the foil. (ii) K.E. of the  $\alpha$ -particle at a distance of  $5 \times 10^{-14} \text{ m}$  from the nucleus, (iii) the shortest distance from the nucleus of silver to which the  $\alpha$ -particle reaches.
- Q.20 Suppose the potential energy between electron and proton at a distance  $r$  is given by . Use Bohr's theory to obtain energy of such a hypothetical atom.
- Q.21 An energy of 68 eV is required to excite a hydrogen like atom from its second Bohr orbit to the third. The nuclear charge is  $Ze$ . Find the value of  $Z$ , the kinetic energy of the electron in the first Bohr orbit and the wavelength of the radiation required to eject the electrons from the first Bohr orbit to infinity.
- Q.23 What is de Broglie wavelength associated with an  $e^-$  accelerated through P.D. = 100 KV.
- Q.24 Calculate the de-Broglie wavelength associated with motion of earth (mass  $6 \times 10^{24} \text{ Kg}$ ) orbiting around the sun at a speed of  $3 \times 10^6 \text{ m/s}$ .
- Q.25 A base ball of mass 200 g is moving with velocity  $30 \times 10^2 \text{ cm/s}$ . If we can locate the base ball with an error equal in magnitude to the  $\lambda$  of the light used ( $5000 \text{ \AA}$ ), how will the uncertainty in momentum be compared with the total momentum of base ball.
- Q.26 An electron has a speed of 40 m/s, accurate up to 99.99%. What is the uncertainty in locating its position?

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### Answer Key

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|      |  |                                   |                                       |                                  |   |
|------|--|-----------------------------------|---------------------------------------|----------------------------------|---|
| Q.1  | 24   | Q.2                               | $182.5 \text{ KJ}$                    | Q.4                              | $331.13 \times 10^4 \text{ J}$          |
| Q.3  | $292.68 \times 10^{21}$ atoms,             | $162.60 \times 10^{21}$ atoms,    | $832.50 \text{ KJ}$                   | Q.6                              | $3.63 \times 10^6 \text{ m}^{-1}$       |
| Q.5  | $h/\pi$                                    | Q.7                               | $938 \text{ \AA}$                     | Q.8                              | $1.35 \times 10^5$                      |
| Q.9  | $8 \times 10^6$                            | Q.10                              | $6530 \times 10^{12} \text{ Hz}$      | Q.11                             | $5 ; 340 \text{ ev} , - 680 \text{ eV}$ |
| Q.12 | $3.09 \times 10^8 \text{ cm/sec}$          | Q.13                              | Brackett ;                            | $2.63 \times 10^{-4} \text{ cm}$ |   |
| Q.14 | $r_n = n = 25 ; 55.2 \text{ pm}$           | Q.15                              | $973.5 \text{ \AA}$                   |                                  |   |
| Q.16 | $10^{22}$                                  | Q.17                              | 47.26%                                | Q.18                             | six , $18800 \text{ \AA}$               |
| Q.19 | $6.4 \times 10^{-13} \text{ J}$ ,          | $2.1 \times 10^{-13} \text{ J}$ , | $3.4 \times 10^{-14} \text{ m}$       | Q.20                             | $E =$                                   |
| Q.21 | $6 ; 489.6 \text{ eV} , 25.28 \text{ \AA}$ | Q.22                              | +1/2 , +1/2 , +1/2 , +3/2 and 2,2,2,4 |                                  |   |
| Q.23 | 3.88 pm                                    | Q.24                              | $3.68 \times 10^{-65} \text{ m}$      |                                  |   |
| Q.25 | $1.75 \times 10^{-29}$                     | Q.26                              | 0.0144 m                              |                                  |   |

## ATOMIC MODELS

Several theories of atomic structure were proposed by different scientists, which are termed as atomic models. These include the Thomson's atomic model, Rutherford's nuclear model, and the Bohr's model.

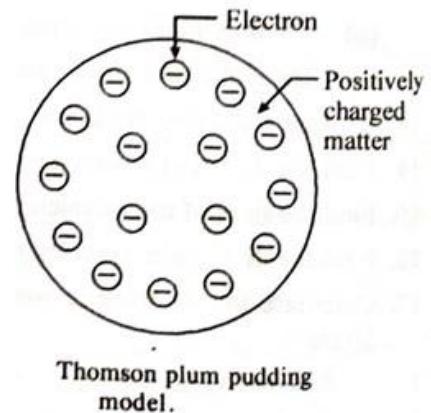
### THOMSON'S ATOMIC MODEL

English physicist J.J. Thomson (1904) was the first to propose the arrangement of the positive charges and negatively charged electrons in an atom. According to Thomson, the entire positive charge of the atom is uniformly distributed within the sphere of atom. The negatively charged electrons are scattered throughout this sphere of positive charge. The condition of electrical neutrality is thus preserved. The electrons are not at rest but are free to move within the cloud of positive charge. This was called Thomson's plum pudding model because the negatively charged electrons (the "plums") are embedded in a sphere of uniform positive charge (the "pudding").

Drawbacks

Thomson's atomic model could not explain the following:

1. Large angle scattering in Rutherford alpha ray scattering experiment.
2. Concept of nucleus of an atom.
3. Origin of spectral lines in case of hydrogen atom.



### RUTHERFORD NUCLEAR MODEL

Rutherford investigated the penetration of alpha particles through matter. A narrow beam of high-energy  $\alpha$ -particles was incident on a thin gold foil. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever, alpha particles struck the screen, a tiny flash of light was produced at that point. The alpha particles scattered in different directions were detected by an  $\alpha$ -particle detector.

Observations:

It was observed that

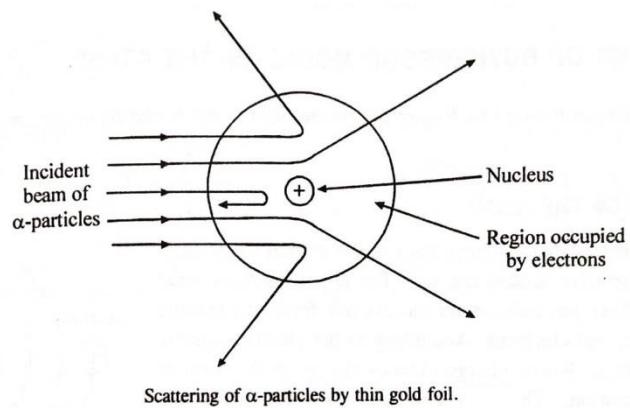
1. Most of the alpha particles passed straight through the gold foil without any deflection.
2. Some of the alpha particles suffered small deflections and were deflected at angles less than  $90^\circ$ .

3. Few alpha particles were deflected through angles more than  $90^\circ$ .
4. A very few alpha particles ( $\sim 1$  in 20,000) were deflected by nearly  $180^\circ$ .

### Explanation

On the basis of the observations, Rutherford concluded that:

1. The large-angle deflection of some alpha particles is due to the strong electrostatic repulsive force exerted by a very small and massive positive point charge that exists at the centre of each gold atom. This very small portion of the atom was called nucleus by Rutherford.
2. Since most of the alpha particles passed straight through the gold foil, this indicated that most of the space in atoms is empty.
3. Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom.



### Proposed Rutherford's Nuclear Model:

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom, according to which:

1. The whole positive charge and entire mass of an atom is concentrated at its centre in a sphere of radius  $10\text{-}14$  m, called the nucleus.
2. The electrons move in circular orbits about the nucleus and the necessary centripetal force is provided by the electrostatic force of attraction between the nucleus and electrons.

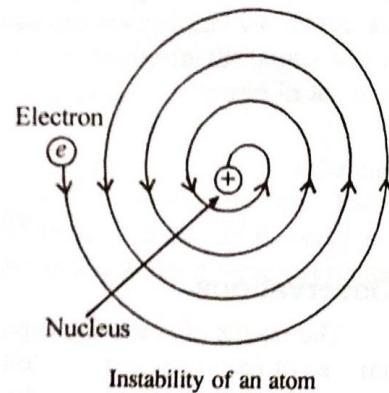
3. Atom is electrically neutral as the total positive charge on the nucleus is equal to the total negative charge of the electrons in the atom.

### DRAWBACKS OF RUTHERFORD MODEL OF THE ATOM

The atomic model put forward by Rutherford on the basis of his scattering experiment had the following limitations:

#### 1. STABILITY OF THE ATOM

Rutherford suggested that the electrons revolve around the nucleus just as the planets revolve around the sun. The electrons move such that the centrifugal force just balances the electrostatic force of attraction between the nucleus and electrons. According to the electromagnetic theory, an accelerating electric charge radiates energy in the form of electromagnetic radiation. The electrons revolving in circular orbits experience a centripetal acceleration and hence should gradually lose energy in the form of electromagnetic radiation. As a result, the electron should approach the nucleus by a spiral path, giving out radiation of a constantly increasing frequency and ultimately falling into the nucleus. Hence, the atom would be highly unstable and would collapse as shown in figure, but in actual practice the atom is stable. This highlights the inadequacy of Rutherford model in explaining the stability of an atom. This contradiction was resolved by Bohr in 1913. He argued that electrons are allowed to move in certain discrete orbits called stationary orbits. An electron cannot radiate any energy while moving in a particular orbit. The emission of radiation takes place only when an electron jumps from one orbit to another orbit of lower energy. Thus in general, the atom remains stable.



#### 2. DISCRETE ATOMIC SPECTRA

According to Rutherford model, the electron spirals gradually towards the nucleus, which results in a constant increase in its angular frequency. Classical approach gives the following expression for the wavelength emitted by an accelerating charge.

$$\lambda = 1/r^{3/2}$$

As  $r$  decreases, the emission wavelength increases continuously. Therefore, the electron should emit electromagnetic radiation of a continuous range of frequencies, resulting in a continuous atomic spectrum.

## Dual nature of electron

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- (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

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

- (4) This can be derived as follows according to Planck's equation,  $E = hv = \frac{hc}{\lambda} \quad (\Theta \quad v = \frac{c}{\lambda})$

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

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

- (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  $4.55 \times 10^{-25} \text{ J}$ . What will be de-Broglie wavelength for this electron

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

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

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

9

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

**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,  $h = 6.626 \times 10^{-27} \text{ erg sec}$

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

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

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

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### **Heisenberg's uncertainty principle**

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(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 , 
$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

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

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

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

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(3) In terms of uncertainty in energy,  $\Delta E$  and uncertainty in time  $\Delta t$ , this principle is written as,

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

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

## Wave mechanical concept – Schrodinger Wave Equation

Erwin Schrodinger developed a wave equation using de-Broglie's theory of particle-wave duality. Schrodinger wave equation describes the behavior of tiny particles such as electrons in terms of waves. The discovery of the Schrodinger wave equation gave a theory from which atomic phenomena such as energy levels of atoms, chemical bonding, and so on could be estimated more correctly and quantitatively. The Schrodinger wave equation describes the wave characteristics of an electron in terms of its position, mass, total energy, and potential energy. The equation is based on a wave function that describes the motion of an electron wave through space.

The Schrodinger wave equation can be written as,

$$\frac{d^2 \Psi}{dx^2} + \frac{d^2 \Psi}{dy^2} + \frac{d^2 \Psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0$$

Where, x, y, z = Space coordinates of the electron wave with respect to the nucleus.

$\nabla^2$  = Laplacian operator

m = mass of the electron

h = Planck's constant

E = Total energy of an electron

V = potential energy of an electron

E - V = kinetic energy of the electron

$\Psi$  = a mathematical function called a wave function. It represents the amplitude of the electron wave surrounding the nucleus at different places in three dimensions. The magnitude that characterizes the de Broglie wave is referred to as the wave function.

## Significance of $\Psi$ and $\Psi^2$

- I.  $\Psi$  is a wave function that refers to the amplitude of an electron wave, i.e. the probability amplitude. It has no physical significance. The wave function could be positive, negative, or imaginary.
  
- II.  $\Psi^2$  is known as probability density determines the possibility of finding an electron at a certain place within the atom. This means that if:

$\Psi^2$  is zero, the chances of finding an electron at that position are negligible.

$\Psi^2$  is high, the probability of discovering an electron is high, indicating that the electron has been there at that location for a long period.

$\Psi^2$  is low, probability of finding an electron is minimal, indicating that the electron is only present for a short period of time.