1.3 SCHRÖDINGER WAVE EQUATION

Erwin Schrödinger proposed that if the electron is wave-like, it should obey the same equation of motion as all other known types of wave motion obey. On the basis of this simple idea, he substituted the value of de-Broglie relation $\left(i.e., \lambda = \frac{h}{mv}\right)$ into the classical equation for wave motion. Thus, the equation obtained should describe the wave motion of the electron and is called *Schördinger wave equation*. The equation can be written in many forms. The simplest form of equation is given below:

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

where E = Total energy of the electron *i.e.*, K.E. + P.E.

V = Potential energy of the electron *i.e.*, work done against the attractive force when the electron moves away from the nucleus.

m = Mass of the electron

h = Planck's constant

The ψ (Greek letter Psi) is called "*Wave function*" and is amplitude of the electromagnetic wave.

The above equation can also be expressed as

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

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is called **Laplacian Operator**.

1.3.1 Derivation of Schrödinger Wave Equation

The simplest form of the equation can be derived by de-Broglie idea of dual nature of matter applied to an electron within all atoms.

Total energy, (E) of an electron = Kinetic energy + Potential energy

$$= \frac{1}{2}mv^2 + \mathrm{V} = \frac{1}{2}\frac{(mv)^2}{m} + \mathrm{V} \qquad \text{...(1.1)}$$

From de-Broglie equation,

$$\lambda = \frac{h}{mv} \quad \text{or} \quad mv = \frac{h}{\lambda}$$

where m is the mass of an electron, v is its velocity, and h is the Planck's constant. Substituting this value of mv in Eqn. (1.1), we get

$$\mathrm{E} = \frac{h^2}{2\lambda^2 m} + \mathrm{V}$$

or

$$+\frac{1}{\lambda^2} = \frac{2m}{h^2}(\mathrm{E}-\mathrm{V}) \qquad \text{...(1.2)}$$

The basic principle of quantum theory is that matter can be regarded as wave and the equation for such a wave motion of a vibrating string can be represented as:

$$\psi = \mathrm{A}\sin\frac{2\pi x}{\lambda} \qquad \text{...(1.3)}$$

where ψ is a wave function, x is the displacement,
λ is the wave length, and A is the amplitude of the wave.

Differentiating the function, ψ, with respect to x, we get

$$\frac{d\psi}{dx} = \mathrm{A}\left(\cos\frac{2\pi x}{\lambda}\right)\left(\frac{2\pi}{\lambda}\right)$$

$$= \mathrm{A}\cdot\frac{2\pi}{\lambda}\cdot\cos\frac{2\pi x}{\lambda}$$

Differentiating again, we get

$$\frac{d^2\psi}{dx^2} = \frac{2\pi\mathrm{A}}{\lambda}\left(-\sin\frac{2\pi x}{\lambda}\right)\left(\frac{2\pi}{\lambda}\right)$$

$$= \frac{-4\pi^2}{\lambda^2}\left(\mathrm{A}\sin\frac{2\pi x}{\lambda}\right)$$

From Eqn. (1.3), we get $\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi$ ...(1.4)

Putting the value of $\frac{1}{\lambda^2}$ from Eqn. (1.2) in the above equation, we have

$$\frac{d^2\psi}{dx^2} = -4\pi^2\psi\left[\frac{2m}{h^2}(\mathrm{E}-\mathrm{V})\right] = \frac{8\pi^2 m}{h^2}(\mathrm{E}-\mathrm{V})\psi$$

Substituting the value of λ from Eqn. (1.2) in eqn. (1.3), we get

$$\frac{d^2\psi}{dx^2} = \frac{8\pi^2 m}{h^2}(\mathrm{E}-\mathrm{V})\psi = 0$$

When the electron moves in three directions x, y and z, the above equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(\mathrm{E}-\mathrm{V})\psi = 0 \qquad \text{...(1.5)}$$

This is the Schrödinger wave equation. It relates the wave function ψ of the electron with its energy E. It is a second order differential equation and can be solved only for certain definite values of energy (E) possessed the electron under reference.

1.3.2 Eigen Values and Eigen Functions

The schrödinger wave equation basically considers the electron motion as the motion of a vibrating string in three directions mutually perpendicular to one another. The motion in one direction can be compared with the motion of a vibrating string between two fixed points. This motion can be represented as a stationary or standing wave shown in the Fig. 1.1. The amplitude is maximum in one direction and then becomes minimum in the same plane in the opposite direction. The position when the amplitude becomes zero is called a *node* and the sign of the wave changes on passing through this nodal point.

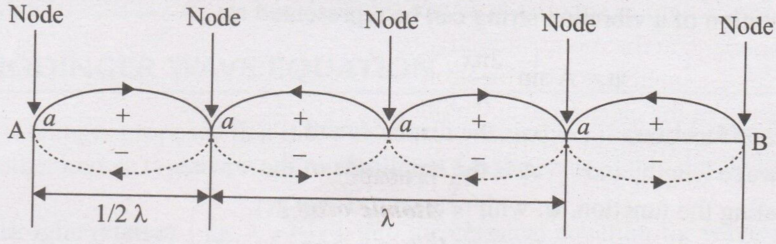


Fig. 1.1 Stationary wave in a vibrating string

Equation (1.4) represents the motion of a stationary wave in one direction, say along the x-axis. It is clear from this equation that for a stationary wave in a stretched string the amplitude function (ψ) can have significance only for a certain definite values of wave length (λ). The wavelength is related to the total energy as $\mathrm{E} = \frac{hc}{\lambda}$. It means energy (E) is a function of the wavelength *i.e.*, each wave having a definite wavelength has a definite value of energy.

Being a second order differential equation, the Schrödinger wave equation can have number of solution, many of them being without any significance. But for some definite values of the total energy E, the solutions will certainly have significant values. *The values of the total energy (E) for which the*

1.4 PARTICLE IN ONE DIMENSIONAL BOX

This is the simplest application of Schrödinger wave equation to the transitional motion of a particle (electron, atom or molecule) in space. The motion of a particle in a one dimensional box is like the flow of electron in a wire, but still it is called ***a particle in a box.*** However, for convenience, we will first derive the result for a particle in one dimensional box and then extend it to a particle in three dimensional box.

Consider a particle which moves along X-axis between $x = 0$ and $x = a$ inside a box. The particle bounces back and forth between the walls of the box, which are considered as rigid. The particle does not lose energy when it collides with the walls, so that its total energy remains constant. From the point of quantum mechanics, potential energy (V) of the particle is infinite on both sides of the box and inside the box V is constant. For convenience, we take V = 0 inside the box. Since the particle cannot possess infinite amount of energy, it cannot exist outside the box, so its wave function ψ is zero for $x \leq 0$ and $x \geq a$.

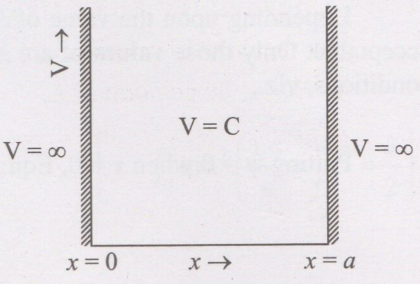


Fig. 1.2 One dimensional potential box

With box, the Schrödinger's wave equation for one dimension:

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2 m}{h^2}(\mathrm{E} - \mathrm{V})\psi = 0 \qquad \text{...(1.7)}$$

where ψ has been taken as the function of x coordinate only.

As outside the box, V = ∞, therefore for outside the box Eqn. (1.7) becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2}{h^2}(\mathrm{E} - \infty)\psi = 0 \qquad \text{...(1.8)}$$

Neglecting E in comparison to ∞, Eqn. (1.8) reduces to

$$\frac{d^2\psi}{dx^2} - \infty\psi = 0$$

or

$$\frac{d^2\psi}{dx^2} = \infty\psi$$

or

$$\psi = \frac{1}{\infty}\frac{d^2\psi}{dx^2} = 0 \qquad \text{...(1.9)}$$

This proves that outside the box $\psi = 0$ which implies that the particle cannot go outside the box, For the particle within the box, V = 0, therefore, the Schrödinger wave equation takes the form

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2}{h^2}\mathrm{E}\,\psi = 0 \qquad \text{...(1.10)}$$

As for the given state of the system, the energy, E is constant (which is one of the postulates of the quantum mechanics), therefore, we put

$$\frac{8\pi^2 m}{h^2}\mathrm{E} = k^2 \qquad \text{...(1.11)}$$

where k^2 is a constant, independent of x.

Equation (1.10), then becomes

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \text{...(1.12)}$$

A general solution of this differential equation is given by

$$\psi = \mathrm{A}\sin kx + \mathrm{B}\cos kx \qquad \text{...(1.13)}$$

where A and B are constants.

Depending upon the value of A, B and k, ψ can have many values. But all the values are not acceptable. Only those values of are acceptable (*i.e.,* are eigen functions) which satisfy the boundary conditions, viz.,

$$\psi = 0 \quad \text{at} \quad x = 0 \quad \text{and} \quad x = a$$

Putting $\psi = 0$ when $x = 0$, Eqn. (1.13) becomes

$$0 = \text{A} \sin 0 + \text{B} \cos 0$$

$$= 0 + \text{B} \qquad [\because \quad \sin 0 = 0 \text{ and } \cos 0 = 1]$$

$$\text{B} = 0$$

Thus, when $x = 0$, Eqn. (1.13) becomes (by putting B = 0),

$$\psi = \text{A} \sin kx \qquad \text{...(1.14)}$$

Now putting $\psi = 0$ when $x = a$, Eqn. (1.14) becomes

$$0 = \text{A} \sin ka$$

$$\sin ka = 0 \qquad \text{...(1.15)}$$

This equation holds good only when the values of ka are integral multiple of it *i.e.,*

$$ka = n\pi \qquad \text{...(1.16)}$$

When n is an integer *i.e.,* $n = 0, 1, 2, 3, ...$ However the value $n = 0$ may be excluded which makes $k = 0$ and hence $\psi = 0$ for any value of 'a' between 0 and a *i.e.,* within the box. This is because the particle is always assumed to be present within the box.

Form Eqn. (1.16)

$$k = \frac{n\pi}{a} \qquad \text{...(1.17)}$$

Substituting this value in Eqn. (1.14), we get

$$\psi = \text{A} \sin\left(\frac{n\pi}{a}x\right) \qquad \text{...(1.18)}$$

This gives the expression for the eigen function ψ.

The expression for the eigen value of the energy may be obtained as follows:

From Eqn. (1.11),

$$\text{E} = \frac{k^2h^2}{8\pi^2\, m} \qquad \text{...(1.19)}$$

Substituting the value of k from Eqn. (1.17), we get

$$\text{E} = \frac{(n\pi / a)^2 h^2}{8\pi^2 m}$$

i.e.,

$$\text{E} = \frac{n^2h^2}{8ma^2} \qquad n = 1, 2, 3, 4, ... \qquad \text{...(1.20)}$$

Equations (1.18) and (1.20) are the solutions of the Schrödinger wave equation for a particle in one-dimensional box. However, the Eqn. (1.18) contains the undetermined constant a, its value can be obtained by the process of normalisation of the wave function as follows:

$$\int_0^a \psi\psi^*\, d\tau = 1$$

Substituting the value of ψ (= ψ *) from Eqn. (1.18), we get

$$A^2 \int_0^a \sin^2 \frac{n\pi}{a} x \, dx = 1$$

or
$$A^2 \frac{a}{2} = 1 \qquad \left[\because \int_0^a \sin^2\left(\frac{n\pi}{a} x\right) dx = \frac{a}{2}\right]$$

or
$$A = \sqrt{\frac{2}{a}}$$

Hence the normalised wave function (which will also be solution of the Schrödinger equation is

$$\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) \qquad ...(1.21)$$

It can be shown that there are any two eigen functions ψ and ψ * corresponding to two different values of n, then ψ_m and ψ_n will be orthogonal to each other.

1.4.1 Some Important Applications for the Study of Particle in One-Dimensional Box

1. **Quantization of energy:** Since n can have only integral values equal to 1, 2, 3 etc., therefore from Eqn. (1.14), it follows that the energy E associated with the motion of a particle in a box can have only discrete values *i.e.,* the energy is quantized. The integer n is called *the quantum number of the particle.* Further putting n = 1, 2, 3.... etc., the discrete energy levels obtained for the particle of mass m confined in the box of length a are shown in Fig. 1.3. It is important to note that as the quantum number increases, the separation between them increases. It may also be noted that energy levels also depends upon the box length a. As a increases *i.e.,* the space available to a particle increases, energy quanta become smaller and energy levels move closer together. Knowing the values of energy of different energy levels, the energy difference between any two levels can be calculated. From the above values, it can be calculated that

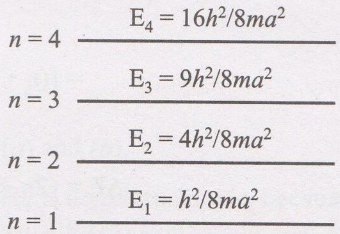


Fig. 1.3 The discrete energy levels of a particle of mass *ma* confined in a box of length *a*

$$E_2 - E_1 = \frac{3h^2}{8ma} \quad \text{and} \quad E_3 - E_2 = \frac{5h^2}{8ma}$$

This shows that the energy difference between any two consecutive (successive) energy levels is not constant.

2. **Existence of zero point energy:** The minimum value of n is 1, therefore the energy corresponding to n = 1, will be minimum and is given by putting n = 1 in Eqn. (1.20), we get

$$E_1 = \frac{h^2}{8ma^2}$$

This shows, when the particle is present in the potential box, the energy of the lowest level (n = 1) is called *zero point energy.* It is characteristic of the system executing to-and-fro motion (vibration) that the energy of their lowest allowed state is greater than zero, *i.e.,* a *zero-point energy exists.*

1.5.2 Concept of Atomic Orbital

In the light of Heisenberg's uncertainty principle, Bohr's concept that the electrons move along definite circular path, lost its significance. Now we can talk of only probability of finding the electron at different points around the nucleus. The probability of finding the electron of a give energy E at any point can be calculated using Schödinger wave equation, *i.e.*, by solving the equation for y corresponding to the co-ordinates of that point and then finding them.

By calculating the probabilities at different points, it is found that there is a three dimensional space around the nucleus. Within which the probability of finding the electron of a given energy is maximum. This space is called an atomic orbital.

Hence an atomic orbital may be defined as a three dimensional space around the nucleus within which the probability of finding the electron of given energy is maximum.

If dots are used to represent the electron probabilities, *i.e.*, a dot represents a point where there is a probability for the electron to be persent, then the orbital corresponding to 1s electron may be represented as shown in Fig. 1.7.

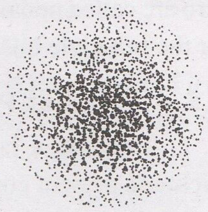


Fig. 1.7 Representation of 1s orbital

Such a representation of an orbital is called *the electron cloud picture*. It may be noted that the intensity of dots which represents the electron probability, is greater near the nucleus and fall off as the distance from the nucleus increase. No where is the probability of finding the electron is equal to zero. Even at large distances from the nucleus, there is a finite, though small, probability of finding an electron of a given energy. This means that electron clouds do not have sharp boundaries. However, for the sake of pictorial clarity and for convenience of representation, a boundary surface may be drawn which encloses a certain, volume of the space around the nucleus within which the probability of finding the electron of a given energy is maximum *i.e.*, 90–95%.

It may be noted that it is not possible to determine the exact position of the electron at any instant of time (in accordance with Heisenberg's uncertainty principal). Hence, the proababilities are calculated in small segments of volume (called volume elements) in space around the nucleus.

1.5.3 Probability Distribution Curves

The curves obtained by plotting the prbabilities (ψ^2) of finding the electron at different distance (r) from the nucleus versus the distances are called probability distribution curves.

It has already been mentioned above that the probability of finding 1*s* electron is maximum near the nucleus and this probability decreases as the distance from the nucleus increases. Hence the probability distribution curve for 1*s* electron is as shown in Fig. 1.8 (*a*). From this curve, it may be further noted that the curve does not touch the *x*-axis even at very large distances showing that the probability does not become zero even at large distances from the nucleus.

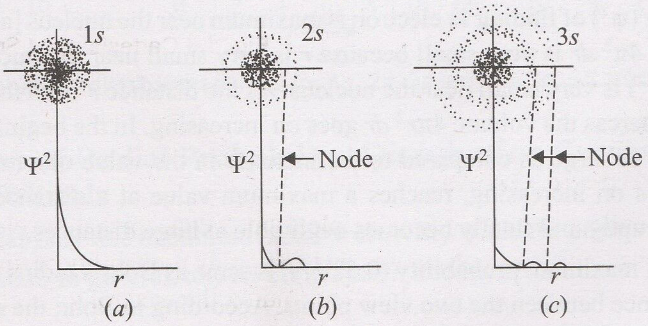


Fig. 1.8 Probability distribution curves for, (*a*) 1*s* (*b*) 2*s* and (*c*) 3*s* orbitals

1.5.6 Radial Probability Distribution Curves for other Orbitals

The radial probability distribution curve for 2*s* orbital consists of two maxima, separated by a region where the radial probability is zero. This region is called a **node**. Thus, the 2*s* orbital has one node. Similarly, 3*s* orbital has three maxima and two nodes. In general, for any *ns* orbital, there are maxima and $(n - 1)$ nodes. Further, it may be seen from the curves that as *n* increases, the distance of maximum radial probability increases but the average electron density decreases as shown by the heights of the humps.

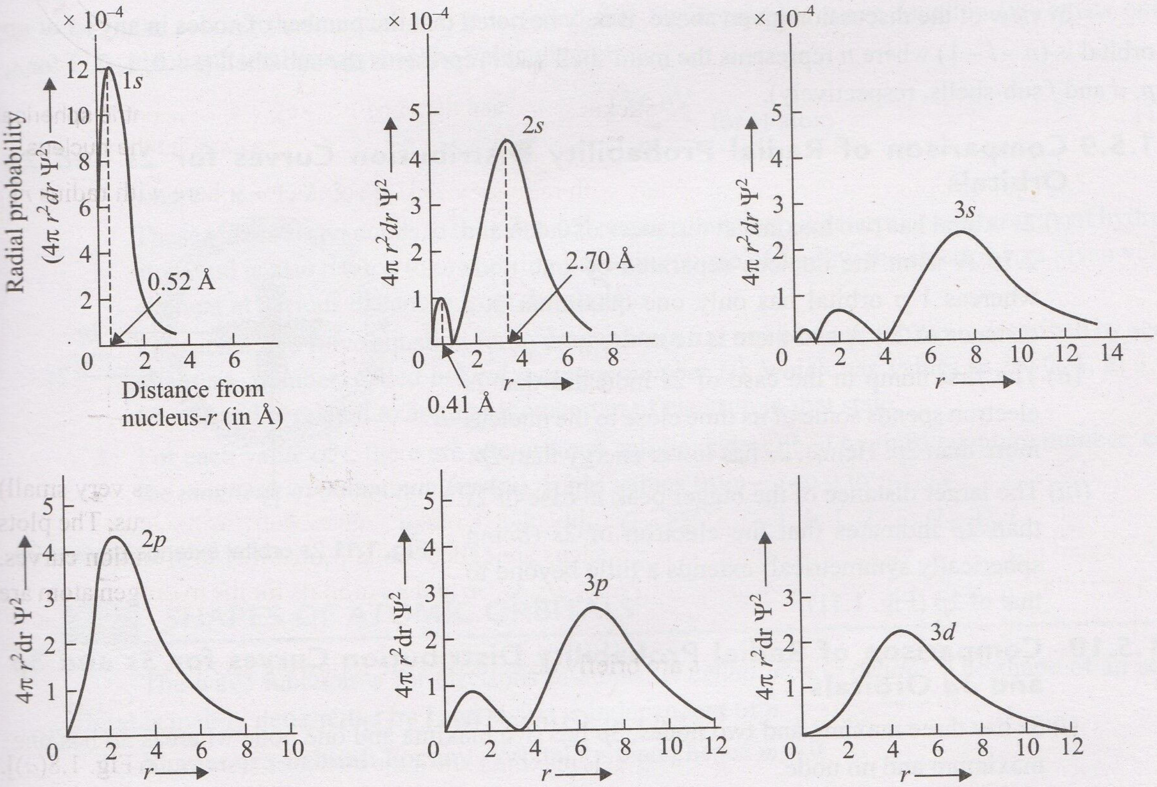
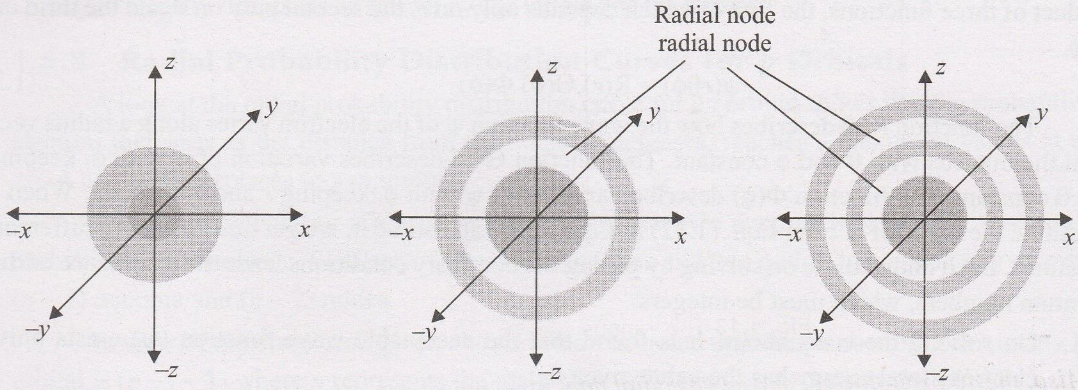


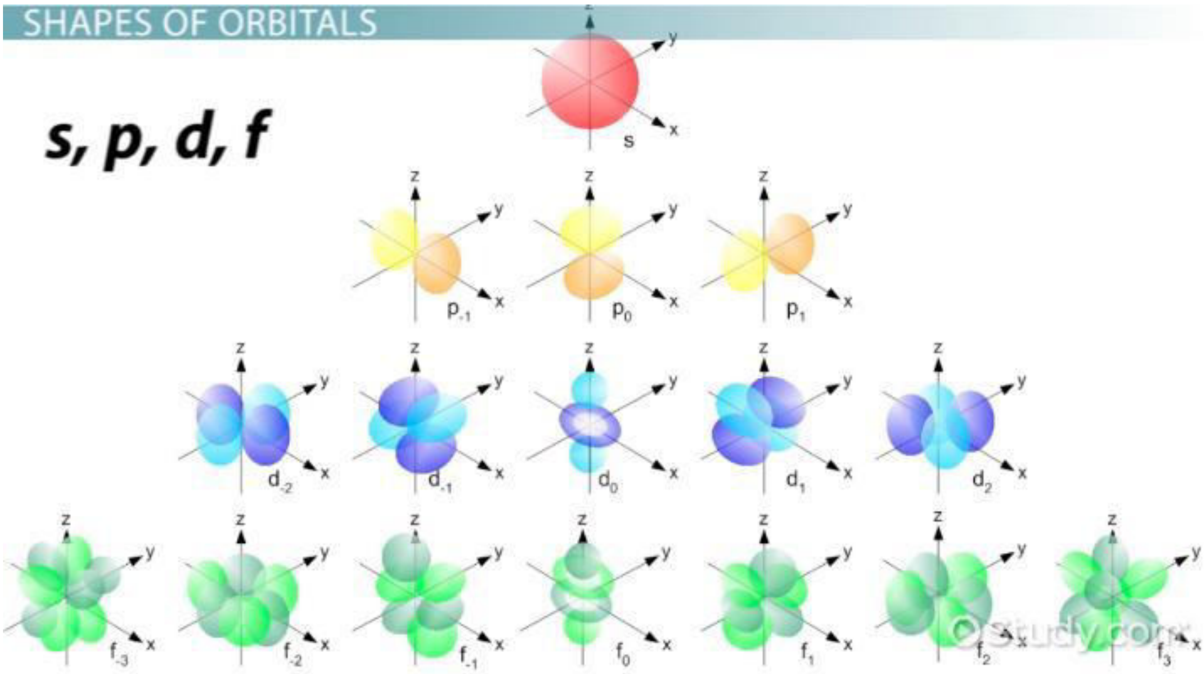
Fig. 1.10 Radial probability distribution curves for 1*s*, 2*s*, 2*p* and 3*s*, 3*p*, 3*d* orbitals of hydrogen atom

summarize this angular independence by saying that 1*s* orbital is **spherically symetrical.** The *s*-orbital has no radial node whereas 2*s* and 3*s* orbitals have one and two radial nodes, respectively, as shown in Fig. 1.12.



(*a*) 1*s*-orbital (*b*) 2*s*-orbitals (*b*) 3*s*-orbitals

Fig. 1.12 The shapes of various *s*-orbitals


SHAPES OF ORBITALS
s, p, d, f
s
p_{-1}
p_0
p_1
d_{-2}
d_{-1}
d_0
d_1
d_2
f_{-3}
f_{-2}
f_{-1}
f_0
f_1
f_2
f_3
x
y
z
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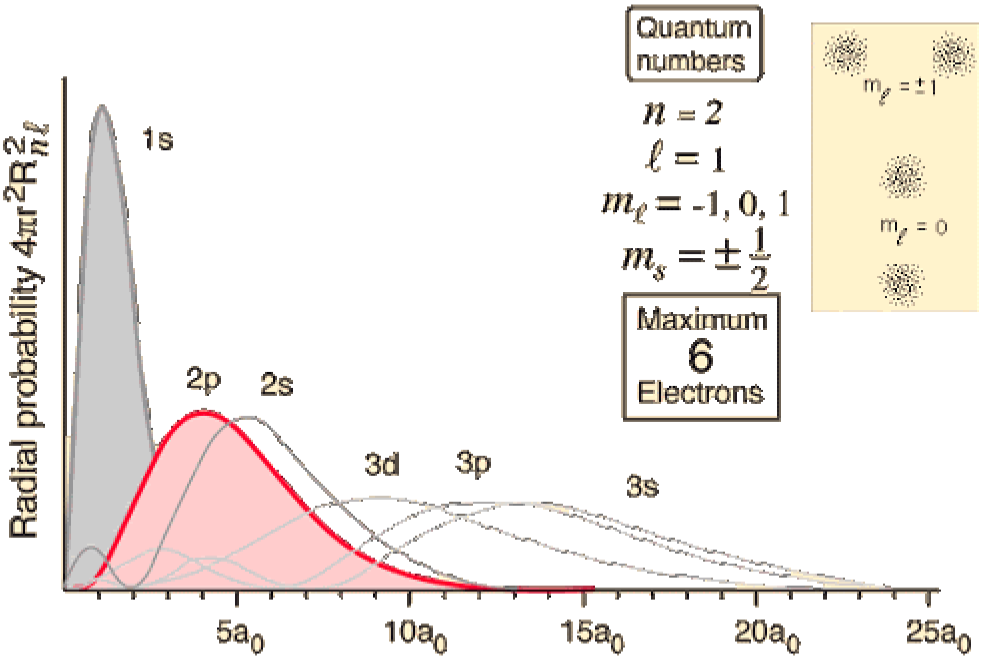
Radial probability $4\pi r^2 R_{n\ell}^2$
1s
2p
2s
3d
3p
3s
$5a_0$
$10a_0$
$15a_0$
$20a_0$
$25a_0$
Quantum numbers
$n = 2$
$\ell = 1$
$m_\ell = -1, 0, 1$
$m_s = \pm\frac{1}{2}$
Maximum 6 Electrons
$m_\ell = \pm 1$
$m_\ell = 0$

3d vs 4s