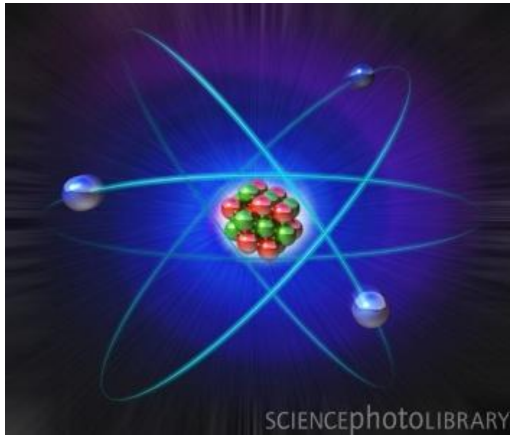
Atomic Structure-II

BSc. 1st Sem (Core)



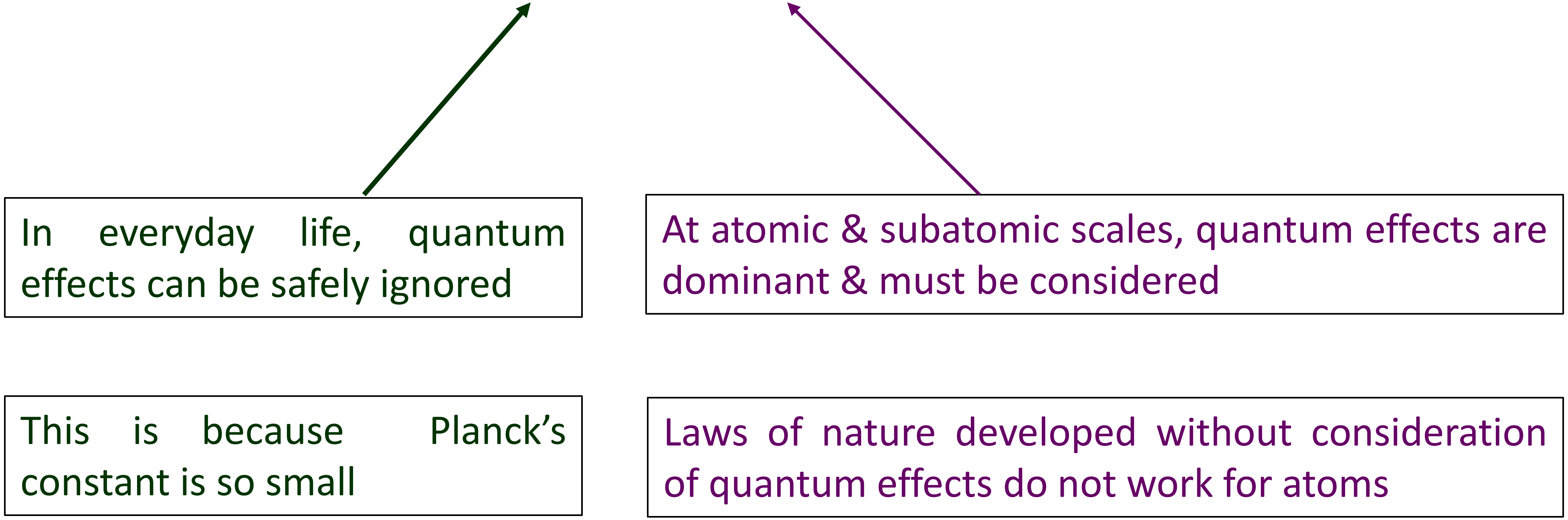
Dr. Bapan Saha

Assistant Professor, Chemistry

Handique Girls' College

Guwahati-01

Classical vs Quantum world



In everyday life, quantum effects can be safely ignored

This is because Planck's constant is so small

At atomic & subatomic scales, quantum effects are dominant & must be considered

Laws of nature developed without consideration of quantum effects do not work for atoms

- Bohr theory fails to cope up with de Broglie hypothesis and Heisenberg's Uncertainty Principle
- A new approach is needed for insight into the structure of the atom.
- This came with the advent of quantum mechanics.

Need for new approach: Quantum Mechanics (QM)

- QM considers the motion of microscopic objects like electron (both wave and particle like).
- Developed independently E. Schrodinger (1926) and W. Heisenberg (1927)
- E. Schrodinger (Noble prize, 1933): Fundamental equation of quantum mechanics.

Wave equation? Schrodinger Equation

- The Schrödinger equation describes the wave properties of an electron in terms of

  - its position

  - mass

  - total energy

  - potential energy
- Most significant feature of the QM: Limits the energies to discrete values (quantized)
- An electron is described by a wave function Ψ, probability of finding the electron at space (atomic orbital).

Schrodinger wave equation

- Schrodinger time independent wave equation is a differential equation which relates the energy of a micro system to its space coordinates
- For an electron having mass m moving in one direction (x-direction) with total energy E, the Schrodinger equation is given by

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

where, Ψ = called wave function, f(x)   V = potential energy, f(x)

h = Planck's constant

- In three dimensions, the equation takes the form,

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

- Two unknown quantities are total energy, E and wave function Ψ
- Numerous solutions of the equations are possible, only few have physical significance.
- Under boundary condition, the energy associated with the electrons become definite.

Schrodinger equation deduction

Considering the particle nature of an electron, the wave equation describing the wave motion of a particle is given by

$$\psi = A\sin 2\pi(x/\lambda) \qquad (1)$$

where; ψ = wave function, A = maximum value of ψ, λ = wavelength of standing wave travelling along x-axis, x = distance of particle from the nucleus

Differentiating (1) with respect to x, we have

$$d\psi/dx = A\cos 2\pi(x/\lambda).(2\pi/\lambda) = (2\pi A/\lambda)\cos 2\pi(x/\lambda) \qquad (2)$$

Again differentiating (2) we have,

$$\begin{aligned} d^2\psi/dx^2 &= (2\pi A/\lambda)\ (-\sin 2\pi(x/\lambda).(2\pi/\lambda) \\ &= -\ (4\pi^2 A/\lambda^2)\sin 2\pi(x/\lambda) \\ &= -\ (4\pi^2/\lambda^2)\ [A\sin 2\pi(x/\lambda)] \\ &= -\ (4\pi^2/\lambda^2)\psi \end{aligned}$$

Thus, $$d^2\psi/dx^2 + (4\pi^2/\lambda^2)\psi = 0 \qquad (3)$$

Equation (3) is the wave motion of any particle along x-axis.

Since electron has both wave and particle nature, equation (3) also represents the wave motion of electron wave along x-axis.

If the electron is considered to move along x, y and z axes,

$$d^2\psi/dx^2 + d^2\psi/dy^2 + d^2\psi/dz^2 + (4\pi^2/\lambda^2)\psi = 0 \qquad (4)$$

Or $\nabla^2\psi + (4\pi^2/\lambda^2)\psi = 0$ where $d^2\psi/dx^2 + d^2\psi/dy^2 + d^2\psi/dz^2 = \nabla^2$, Laplacian operator

Or $(4\pi^2/\lambda^2)\psi = - \nabla^2 \psi$

Or $(1/\lambda^2) = - \nabla^2 \psi\ (1/4\pi^2\psi) \qquad (5)$

According to de Broglie, $\lambda = h/mv$ and using it in equation (5) we have

$$m^2v^2/h^2 = - \nabla^2 \psi\ (1/4\pi^2\psi)$$

Or $\frac{1}{2} mv^2 = - \nabla^2 \psi\ (h^2/8\pi^2\psi m)$

Or $KE = - \nabla^2 \psi\ (h^2/8\pi^2\psi m)$

Or $\nabla^2 \psi + (8\pi^2 m/h^2)KE\psi = 0 \qquad (6)$

Potential Energy (V) for an electron moving in a field of a positive nucleus is not constant, can also vary.

Total energy, E = PE + KE and thus KE = E – V, using it in equation (6) we have

$$\nabla^2 \psi + (8\pi^2 m/h^2)(E - V)\psi = 0 \qquad (7)$$

Equation (7) is known as Schrodinger wave equation

Or $\nabla^2 \psi + (8\pi^2 m/h^2)(E + e^2/r)\,\psi = 0$, where $V = -\,e^2/r$ (H-atom) (8)

Or $\nabla^2 \psi = -\,(8\pi^2 m/h^2)(E\psi + e^2\psi/r)$

Or $(-\,h^2/8\pi^2 m)[\nabla^2 \psi] = (E\psi + e^2\psi/r)$

Or $[(-\,h^2/8\pi^2 m)[\nabla^2 - e^2/r]\psi = E\psi$

Or $H\psi = E\psi$ (9)

where $H = [(-\,h^2/8\pi^2 m)[\nabla^2 - e^2/r]$ = Hamiltonian operator = Sum of potential (V) and kinetic energy operator (T)

Equation (9) is the Schrodinger wave equation for a system whose energy does not change with time (time independent)

Operator: ^ is a symbol or expression that suggests to do something to what it follows it.

For H-like atom (He^+ of Li^{2+}) replace e^2 with Ze^2 (Z=atomic number)

Eigen functions and Eigen values

- Schrodinger wave equation for a system whose energy does not change with time (time independent) is given by

$$H\psi = E\psi$$

where $H = [(- h^2/8\pi^2 m)[\nabla^2 - e^2/r]$ = Hamiltonian operator, also known as energy operator

- The particular values of Ψ which gives satisfactory solution of Schrodinger equation are called eigen functions and corresponding energy values are called eigen values for the system under consideration.
- In Schrodinger equation, H operates on Ψ to give E times Ψ, and Ψ is an eigen function and E obtained is the eigenvalue.
- When an operator O operates on a function Ψ_n to give back the function multiplied by some constant an i.e., operator (function) = constant x same function

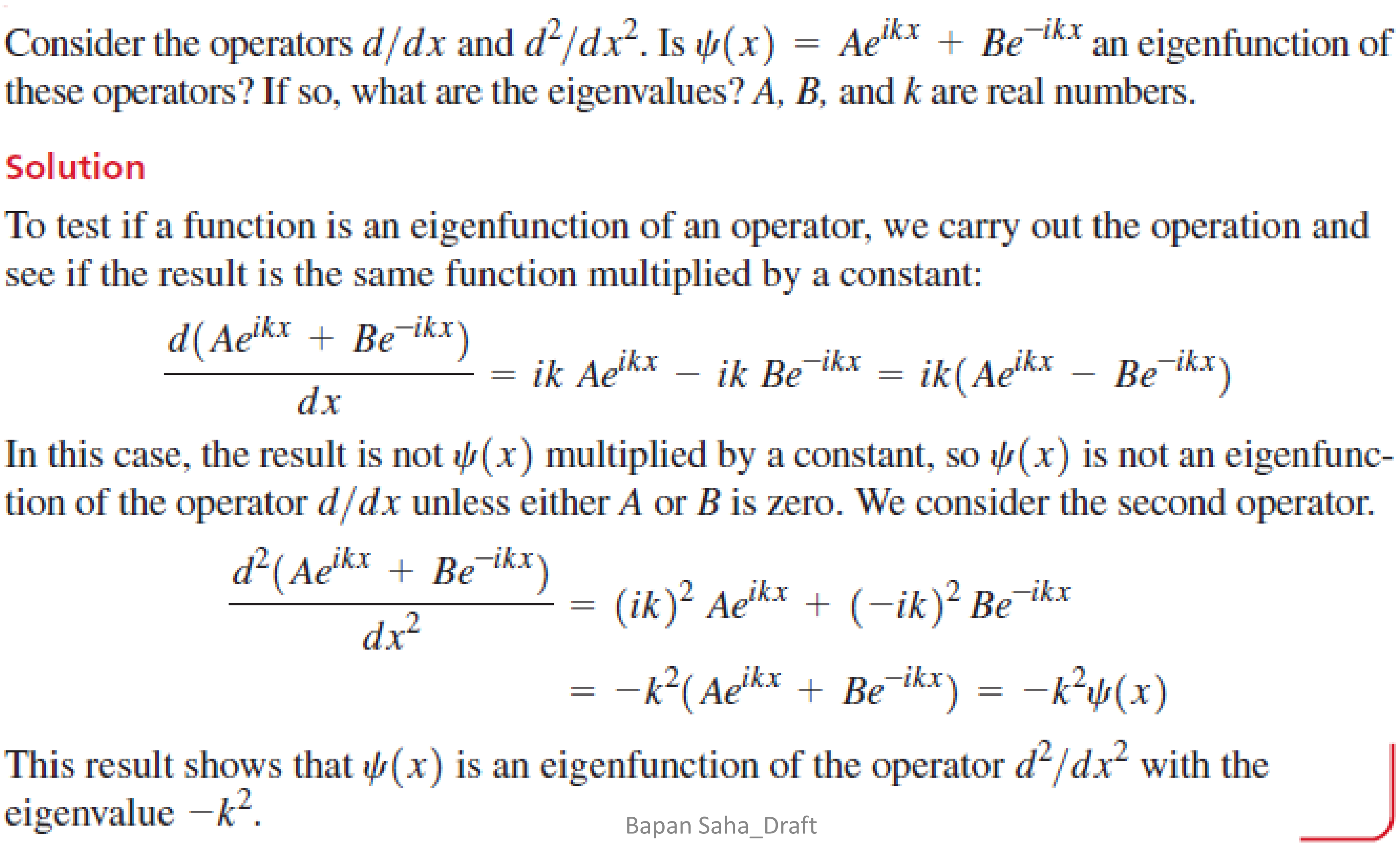
$$\hat{O}\psi_n = a_n \psi_n$$

Ψ_n is known to be an eigenfunction of the operator and an is its corresponding eigenvalue

- The operator acting on these special wave functions returns the wave function multiplied by a number. These special functions are called the eigenfunctions of the operator and the a_n are called the eigenvalues.

Eigen means appropriate

- The eigenvalues for quantum mechanical operators are always real numbers because they correspond to the values of observables that are measured in an experiment.
- There are in general an infinite number of eigenfunctions for a given operator for the specific system under consideration.



Consider the operators d/dx and d^2/dx^2. Is $\psi(x) = Ae^{ikx} + Be^{-ikx}$ an eigenfunction of these operators? If so, what are the eigenvalues? A, B, and k are real numbers.

Solution

To test if a function is an eigenfunction of an operator, we carry out the operation and see if the result is the same function multiplied by a constant:

$$\frac{d(Ae^{ikx} + Be^{-ikx})}{dx} = ik\,Ae^{ikx} - ik\,Be^{-ikx} = ik(Ae^{ikx} - Be^{-ikx})$$

In this case, the result is not $\psi(x)$ multiplied by a constant, so $\psi(x)$ is not an eigenfunction of the operator d/dx unless either A or B is zero. We consider the second operator.

$$\begin{aligned}\frac{d^2(Ae^{ikx} + Be^{-ikx})}{dx^2} &= (ik)^2\,Ae^{ikx} + (-ik)^2\,Be^{-ikx}\\ &= -k^2(Ae^{ikx} + Be^{-ikx}) = -k^2\psi(x)\end{aligned}$$

This result shows that $\psi(x)$ is an eigenfunction of the operator d^2/dx^2 with the eigenvalue $-k^2$.

Characteristics of Wave Function: What Prof. Born Said ?

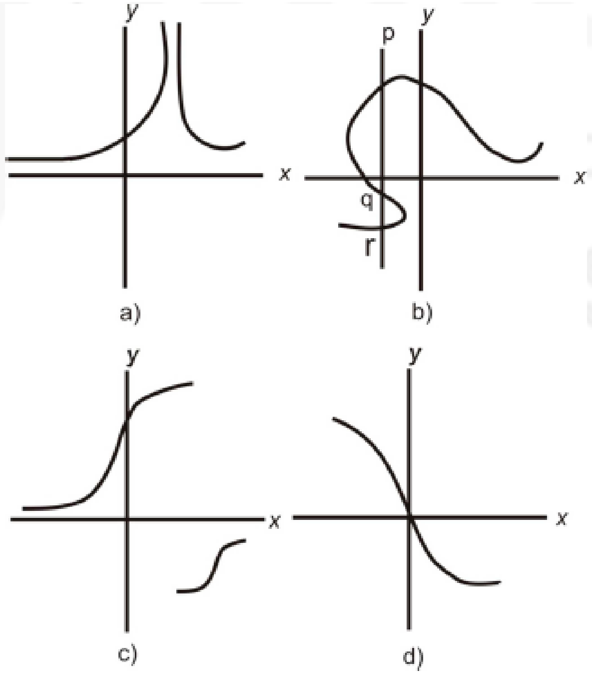
- Heisenberg’s Uncertainty principle: We can never know exactly where the particle is.
- Our knowledge of the position of a particle can never be absolute.
- In Classical mechanics, square of wave amplitude is a measure of radiation intensity
- In a similar way, ψ^2 or $\psi\psi^*$ may be related to density or appropriately the probability of finding the electron in the space.

Physical significance of wave function (Ψ)

- Wave function Ψ can be regarded as an amplitude function for a wave
- It can have both positive and negative values
- The wave function Ψ has to describe some property of electron, atomic orbital
- The square of wave function, Ψ^2 is more meaningful.
- Ψ^2 is proportional to the probability of finding an electron in a given region of space at any instant (not equal to probability).
- If Ψ is a complex, $\Psi\Psi^*$ is preferably used instead of Ψ^2.
- When an electron is confined in a particular region of space $d\tau$ (= dxdydz, volume element), the probability of finding an electron in this region can be given by integration $\int_{-\alpha}^{\alpha} \Psi\Psi^* d\tau = 1$
- The total probability of locating the electron must be unity $\int_{-\alpha}^{\alpha} \Psi\Psi^* d\tau = 1$
- $\Psi\Psi^*$ is known as the probability density of the electron

Conditions for well behaved function (required for realistic solution)

- Ψ must be single valued - There cannot be two probabilities for an electron at any position in space
- Ψ must be continuous - The probability must be defined at all positions in space and cannot change abruptly from one point to the next
- Ψ must be finite and approach zero at infinity - For large distances from the nucleus, the probability must grow smaller and smaller (the atom must be finite).
- Ψ in Fig (a) is not well behaved because it is not finite
- Ψ in Fig (b) is not well behaved because it is not single valued for a particular value of x (three values p, q and r)
- Ψ in Fig (c) is not well behaved because it is not continuous
- Ψ in Fig (a) is well behaved because it is single valued, finite and continuous



Pictorial representation of wave functions; the curves a), b) and c) represent the functions which are not well behaved while d) shows the well behaved function.

Postulates of quantum mechanics

1. The state of a quantum mechanical particle is completely specified by a wave function Ψ (x, t)
2. For every measurable property of a system (position, momentum, energy) there exists a corresponding operator in quantum mechanics.
3. In any single measurement of the observable that corresponds to the operator O, the only values that will ever be measured are the eigenvalues of that operator.
4. If the system is in a state described by the wave function Ψ (x, t), then the average value (expectation value) of the observable corresponding to *A* is given by

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A} \psi \, d\tau$$

5. The wavefunction of a system evolves in time according to time dependent Schrodinger equation.

$$\hat{H}\Psi(x,t) = i\hbar \frac{\partial}{\partial t}\psi(x,t)$$

In time dependent Schrodinger equation the Hamiltonian and the wavefunction depend on time also

Normalized and orthogonal wave functions

- The total probability of an electron being *somewhere* in space = 1. This is called normalizing the wave function.

$$\int_{-\alpha}^{\alpha} \Psi\Psi^{*} d\tau = 1$$

- If the function is not normalized, it can be done by multiplication of the wave function by a constant N (normalization constant) such that $\int_{-\alpha}^{\alpha} N^2\Psi\Psi^{*} d\tau = 1$ or $N^2\int_{-\alpha}^{\alpha} \Psi\Psi^{*} d\tau = 1$
- Normalization constant ensures that probability of finding the electron is unity, not just proportional to it
- Orthogonal functions are completely independent functions and one can not be expressed in terms of other.

$$\int_{-\alpha}^{\alpha} \Psi\Psi^{*} d\tau = 0$$

- A wave function is mutually orthogonal to each other if it satisfies the above condition
- All orbitals in an atom must be orthogonal to each other.

Normalize the function $a(a - x)$ over the interval $0 \leq x \leq a$.

Solution

To normalize a function $\psi(x)$ over the given interval, we multiply it by a constant N, and then calculate N from the equation $N^2 \int_0^a \psi^*(x)\psi(x)\,dx = 1$.

In this particular case,

$$N^2 \int_0^a [a(a - x)]^2\,dx = 1$$

$$N^2 a^2 \int_0^a [a^2 - 2ax + x^2]\,dx = 1$$

$$N^2\left(a^4 x - a^3 x^2 + a^2 \frac{x^3}{3}\right)_0^a = 1$$

$$N^2 \frac{a^5}{3} = 1 \text{ so that } N = \sqrt{\frac{3}{a^5}}$$

The normalized wave function is $\sqrt{\frac{3}{a^5}}\,a(a - x)$

Some observables and their operators

Name	Observable Symbol	Operator Symbol	Operation
Position	x	$\hat{X}$	Multiply by x
	r	$\hat{R}$	Multiply by r
Momentum	P_x	$\hat{P}_x$	$-ih\frac{\partial}{\partial x}$
	P	$\hat{P}$	$-ih\left(i\frac{\partial}{\partial x}+j\frac{\partial}{\partial y}+k\frac{\partial}{\partial z}\right)$
Kinetic energy	K_x	$\hat{K}_x$	$-\frac{h^2}{2m}\frac{\partial^2}{\partial x^2}$
	K	$\hat{H}$	$-\frac{h^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	$U(x)$	$U(\hat{x})$	*Multiply by* $U(x)$
	$U(x,y,z)$	$U(\hat{x},\hat{y},\hat{z})$	*Multiply by* $U(x,y,z)$
Total energy	E	$\hat{H}$	$-\frac{h^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$ $+U(x,y,z)$
Angular momentum	$l_x = yp_z - zp_y$	$\hat{L}_x$	$-ih\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	$l_y = zp_x - xp_z$	$\hat{L}_y$	$-ih\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	$l_z = xp_y - yp_x$	$\hat{L}_z$	$-ih\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

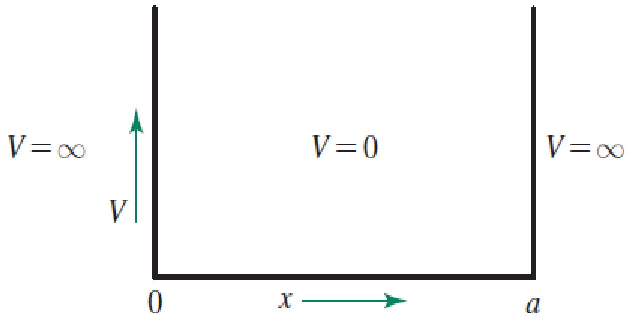
Energy states of the H-like atoms

- The solution of Schrodinger equation for H-atom $\left[\frac{-h^2}{8\pi^2 m}\nabla^2 + V\right]\psi = E\psi$

  gives the expression of energy E as $E = \frac{-Z^2 e^4 \mu}{8\,\epsilon_0\,h^2 n^2}$ where n=1, 2, 3,……..
- Mass of the nucleus (M) is much larger than that of an electron (m) hence μ [reduced mass = mM/(m+M)] can be replaced by m.
- The energy expression becomes $E = \frac{-Z^2 e^4 m}{8\,\epsilon_0^2\,h^2 n^2}$ (identical to the energy obtained from Bohr's theory)
- Since the expression does not involve l and m_l, the levels given by a certain value of n are degenerate.
- The values of n^2 gives the degeneracy of the nth energy level
- For example, where n=1 there is only one energy level and this corresponds to 1s level
- When n=2, degeneracy is $n^2=4$ and hence 2s and three 2p orbitals are degenerate
- When n=3, degeneracy is $n^2=9$ and hence 3s, three 3p and five 3d (nine) orbitals are degenerate

Particle in 1-D box

- Consider a particle of mass m moving back and forth between the walls of a 1D box.
- The potential energy $V(x)$ inside the box, between $x = 0$ and $x = a$, is zero and outside it is infinite.
- It means that the particle is completely trapped in the box and would require an infinite amount of energy to leave it.
- Thus the potential function is $V(x) = 0;\ 0 < x < a$ & $V(x) = \alpha;\ 0 \geq x \geq a$



Potential Energy Well for the Particle in a Box

- Here the particle cannot move outside and the boundary conditions can be written as

$$\Psi = 0 \text{ at } x=0 \ \& \ \Psi \neq 0 \text{ at } 0 \leq x \leq 0$$

- The Schrodinger's equation in 1D is

$$d^2\psi/dx^2 + (8\pi^2 m/h^2)(E - V)\,\psi = 0$$

Or $$d^2\psi/dx^2 + (8\pi^2 m/h^2)E\psi = 0 \qquad (1) \qquad \text{(since V=0)}$$

- The wave characteristics of a particle is described by a combination of sine and cosine functions.
- A general solution to above equation in the box will be

$$\Psi(x) = A \sin kx + B \cos kx \qquad (2) \qquad \text{A and B are constants}$$

- Substitution into the wave equation allows solution for k

$$k^2 = 8\pi^2 mE/h^2 \qquad (3)$$

- Applying boundary condition,

at $x=0$ $\quad \Psi(x) = 0 = A \sin kx + B \cos kx$

Or $\quad B = 0$

Thus, $\quad \Psi(x) = A \sin kx$

at $x=a$ $\quad \Psi(x) = 0 = A \sin ka$

Or $\quad \sin ka = 0 \qquad (A \neq 0)$

Or $\quad ka = n\pi$

Or $\quad k = n\pi/a \qquad (4)$

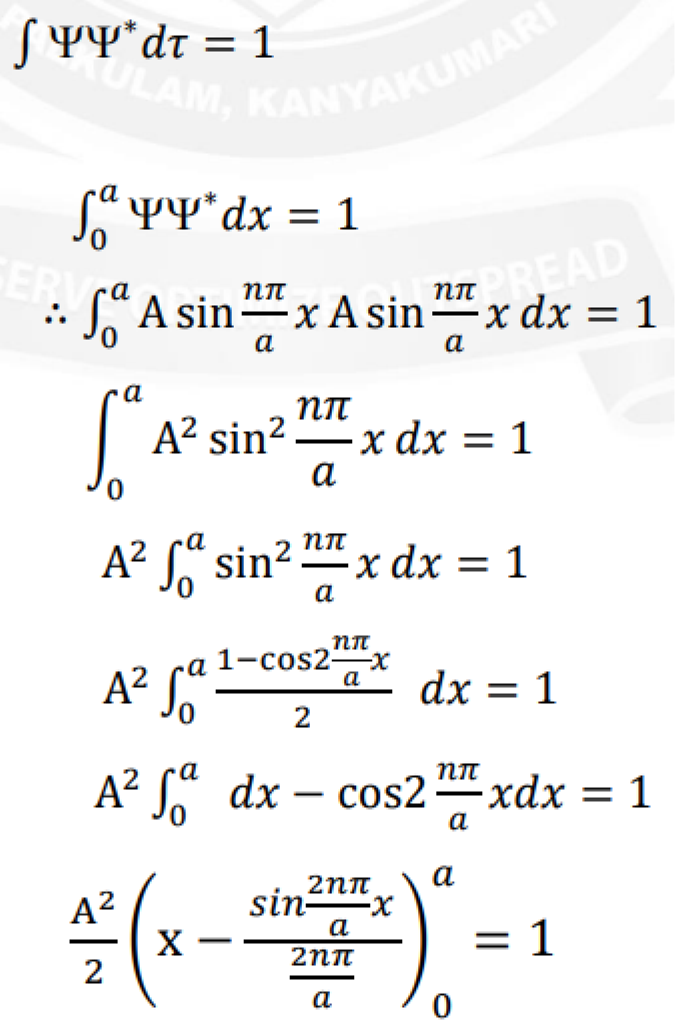
Using equation (4) in equation (3) we have

$$8\pi^2 mE/h^2 = n^2\pi^2/a^2$$

Or $\quad E = n^2h^2/8ma^2 \qquad (5)$

This is the expression for energy Eigen value for a particle moving in 1D box

- To find energy Eigen function $\Psi(x) = A\sin kx = A\sin(n\pi/a)x$
- Normalisation of wave function
- Within the potential well the particle is present, then the probability of finding the particle is



$$\int \Psi\Psi^* d\tau = 1$$

$$\int_0^a \Psi\Psi^* dx = 1$$

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

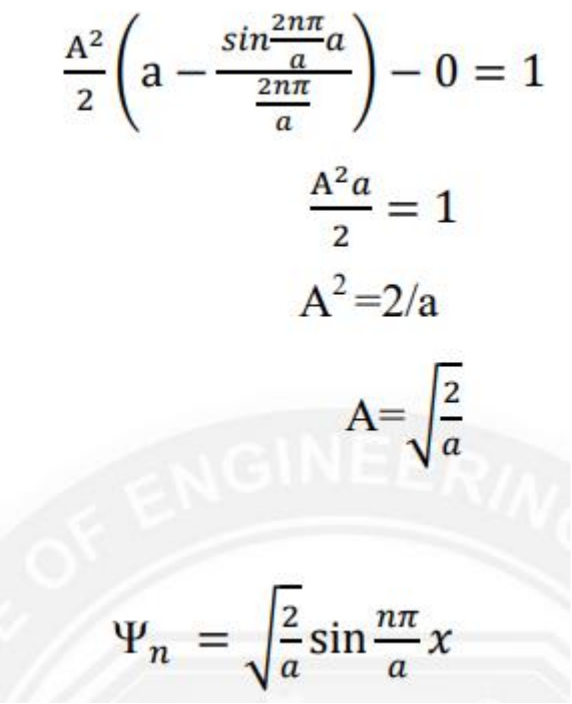
$$\int_0^a \mathrm{A}^2\sin^2\frac{n\pi}{a}x\,dx = 1$$

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

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

$$\mathrm{A}^2\int_0^a dx - \cos 2\frac{n\pi}{a}xdx = 1$$

$$\frac{\mathrm{A}^2}{2}\left(\mathrm{x} - \frac{\sin\frac{2n\pi}{a}x}{\frac{2n\pi}{a}}\right)_0^a = 1$$



$$\frac{\mathrm{A}^2}{2}\left(\mathrm{a} - \frac{\sin\frac{2n\pi}{a}a}{\frac{2n\pi}{a}}\right) - 0 = 1$$

$$\frac{\mathrm{A}^2 a}{2} = 1$$

$$\mathrm{A}^2 = 2/\mathrm{a}$$

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

$$\Psi_n = \sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x$$

This is the expression for Eigen function or wave function of a particle moving in a 1D potential well.

- The nature of plot of wave function (Ψ_n) and their corresponding probability densities (Ψ_n^2) for n = 1, 2, 3 are shown below
- Ψ_n may be both positive and negative, but Ψ_n^2 is always positive
- For each Ψ_n, the length of the box should contain an integral number of half wavelengths
- For n=1, the most probable position of the particle is at a/2
- For n=2, this point corresponds to a node (probability of finding the particle at the point becomes zero)
- For every Ψ_n, there are n-1 nodes in addition to those at the boundaries (high probability on either side of these nodes)
- Energy levels are quantized $E = n^2h^2/8ma^2$ (n=1, 2, 3….) Since n cannot be zero, the particle in the box has minimum energy $E_o = h^2/8ma^2$ (zero point energy or residual energy)

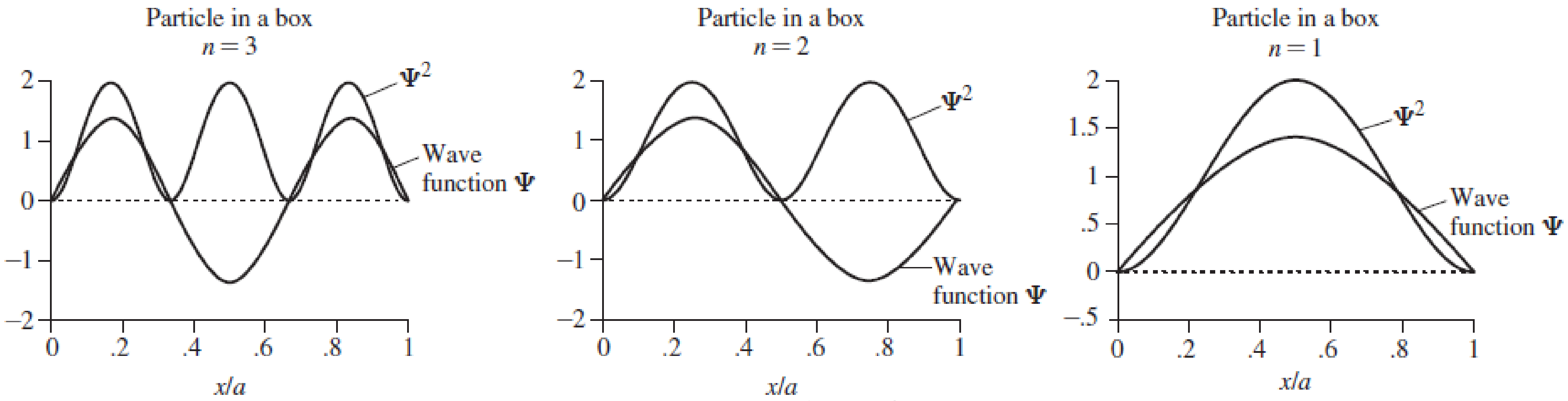


FIGURE 2.4 Wave Functions and Their Squares for the Particle in a Box with $n = 1, 2,$ and 3.

- Energy Eigen value is inversely proportional to the square of width of the potential well.
- Energy Eigen value is inversely proportional to the mass of the particle.
- The probability of finding the particle is maximum at the center for the first energy value.
- The probability of finding the particle is minimum at the centre for the second energy value.
- The squared wave functions are the probability densities (varied probabilities at different locations in the box.)
- The sign of ψ has no direct physical significance (both positive/negative regions shows same probability distribution).
- The probability of finding the particle between x and (x+dx) is proportional to ψψ*dx, probability density
- The energy of particle depends directly on n^2
- As n increases, the successive energy levels get closer and closer and ultimately merged into a continuum

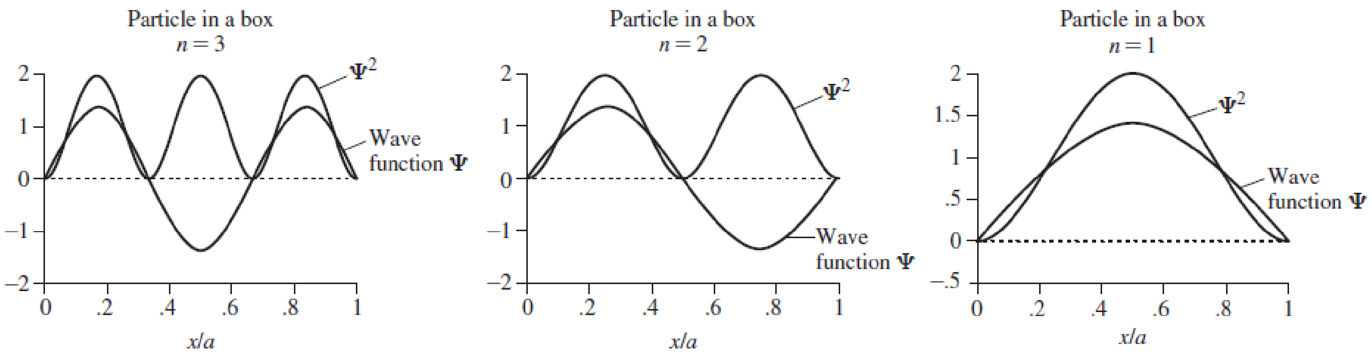


FIGURE 2.4 Wave Functions and Their Squares for the Particle in a Box With $n = 1, 2$, and 3

Schrodinger equation in polar coordinate (H-atom)

- In H- and H-like atoms, an electron moving in the force field of the nucleus.
- There is coulomb attraction between a fixed nucleus of charge Ze and mass M and a moving electron of charge e and mass m.
- The PE of this system is given by $V = \frac{-Ze^2}{4\pi \in_0 r}$
- The reduced mass μ of the electron is given by $\mu = \frac{mM}{m+M}$
- The Schrodinger equation for H- and H-like atoms is thus $\nabla^2\psi + \frac{8\pi^2\mu}{h^2}(E + \frac{Ze^2}{4\pi \in_0 r})\psi = 0$
- The only successful attempts to find solutions of the wave equation have been those in which position of electron is given in polar coordinates.
- Cartesian coordinate $\Psi(x, y, z)$ may be expressed in terms of spherical coordinate $\Psi(r, \theta, \phi)$.
- Spherical coordinate *r* represents the distance from the nucleus
- θ is the angle between radius vector and *z* axis (Zenith angle, varying from 0 to π)
- ϕ is the angle between radius vector on xy-plane and *x* axis (Azimuth angle, varying from 0 to 2π).

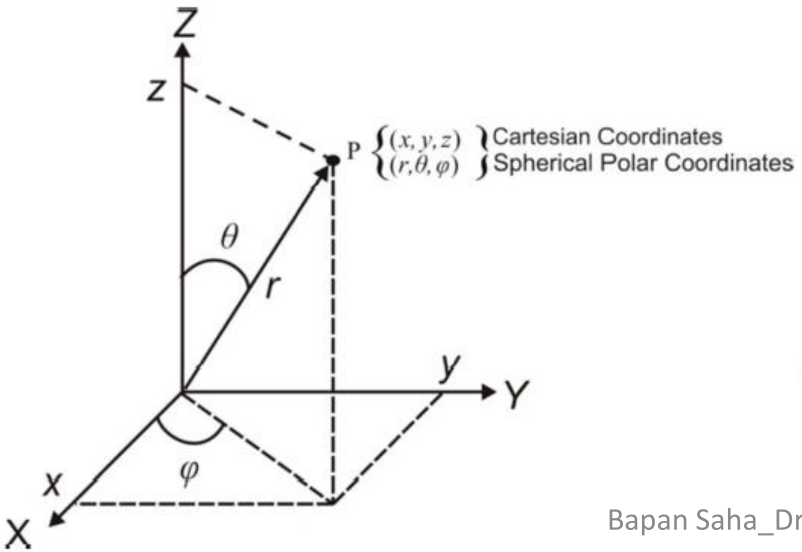
- Conversion of Cartesian to spherical coordinates is carried out as;

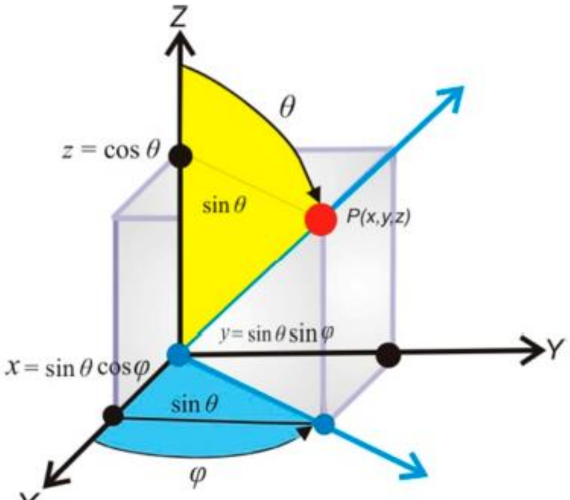
$x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, $z = r\cos\theta$ and $r = [x^2 + y^2 + z^2]^{1/2}$

- Schrodinger equation for H-atom can be expresses in spherical polar coordinates r, θ, ϕ as follows

$$\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2}+\frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\psi}{\partial\theta})$$
$$+\frac{8\pi^2\mu}{h^2}(E+\frac{Ze^2}{4\pi\epsilon_0 r})=0 \qquad \ldots$$

- Accordingly, the solution of the above Schrodinger equation i.e., wavefunction is given as Ψ (r, θ, ϕ) = R(r). $\Theta(\theta)$. $\Phi(\phi)$ where R(r) and $\Theta(\theta)$. $\Phi(\phi)$ are known as radial and angular part of the wavefunction





- The Schrodinger equation in the polar form has an advantage: One can express as a product of three functions that depends only on r, θ *and* ϕ

$$\Psi\ (r, \theta, \phi) = R(r).\ \Theta(\theta).\ \Phi(\phi)$$

- Thus, Ψ can be factored into a radial component and two angular components.
- The radial function R describes electron density at different distances from the nucleus;
- The angular functions describe the shape of the orbital and its orientation in space.
- The two angular factors are sometimes combined into one factor, called Y

Solution of Schrodinger wave equation for H-atom

- Solution of Schrodinger wave equation (polar coordinates) may be described as

$$\Psi(r, \theta, \phi) = R(r).\ \Theta(\theta).\ \Phi(\phi) \qquad (1)$$

where; R(r) is a function that depends on the distance from the nucleus, which in turn depends on principal (n) & azimuthal (l) quantum numbers

$\Theta(\theta)$ is a function of θ, depends on the azimuthal (l) & magnetic (m) quantum numbers

$\Phi(\phi)$ is a function of ϕ, which depends only on the magnetic (m) quantum number

- Equation (1) can be described as the product of two functions

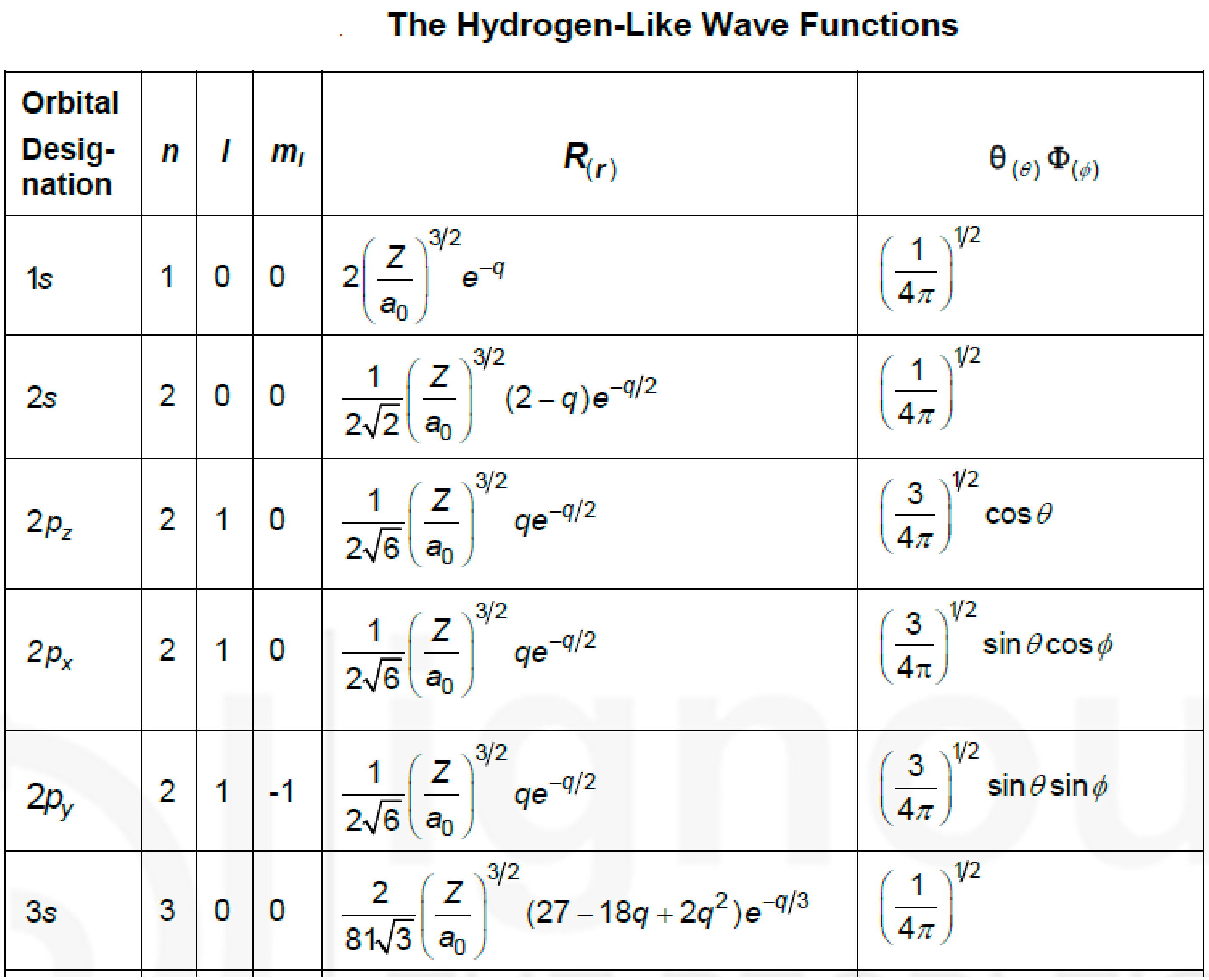
$$\Psi(r, \theta, \phi) = R(r)_{n,l}.Y(\theta, \phi)_{l,m} \qquad (2)$$

where; $R(r)_{n,l}$ is called the radial part and $Y(\theta, \phi)_{l,m}$ is angular part of wavefunction $\Psi(r, \theta, \phi)$

- This splits the wavefunction into two parts which can be solved separately: $R(r)_{n,l}$ depends on principal (n) and azimuthal (l) quantum numbers and $Y(\theta, \phi)_{l,m}$ depends on azimuthal (l) and magnetic (m) quantum numbers
- The wavefunction of the electron in the hydrogenic atom is called an atomic orbital.
- An orbital is a one electron wavefunction

The radial wave function

- Radial function depends on *n* and *l*
- Angular function depends on *m* and *l*
- All orbitals decay exponentially with sufficient increase in distances from the nucleus.
- Some orbitals oscillate through zero close to the nucleus and have one or more radial nodes before beginning their final exponential decay.
- The wave function of an orbital with higher n extends to a larger distance from the nucleus
- A node is a surface where wave function passes through zero as it changes sign
- Besides radial nodes, there are also angular node

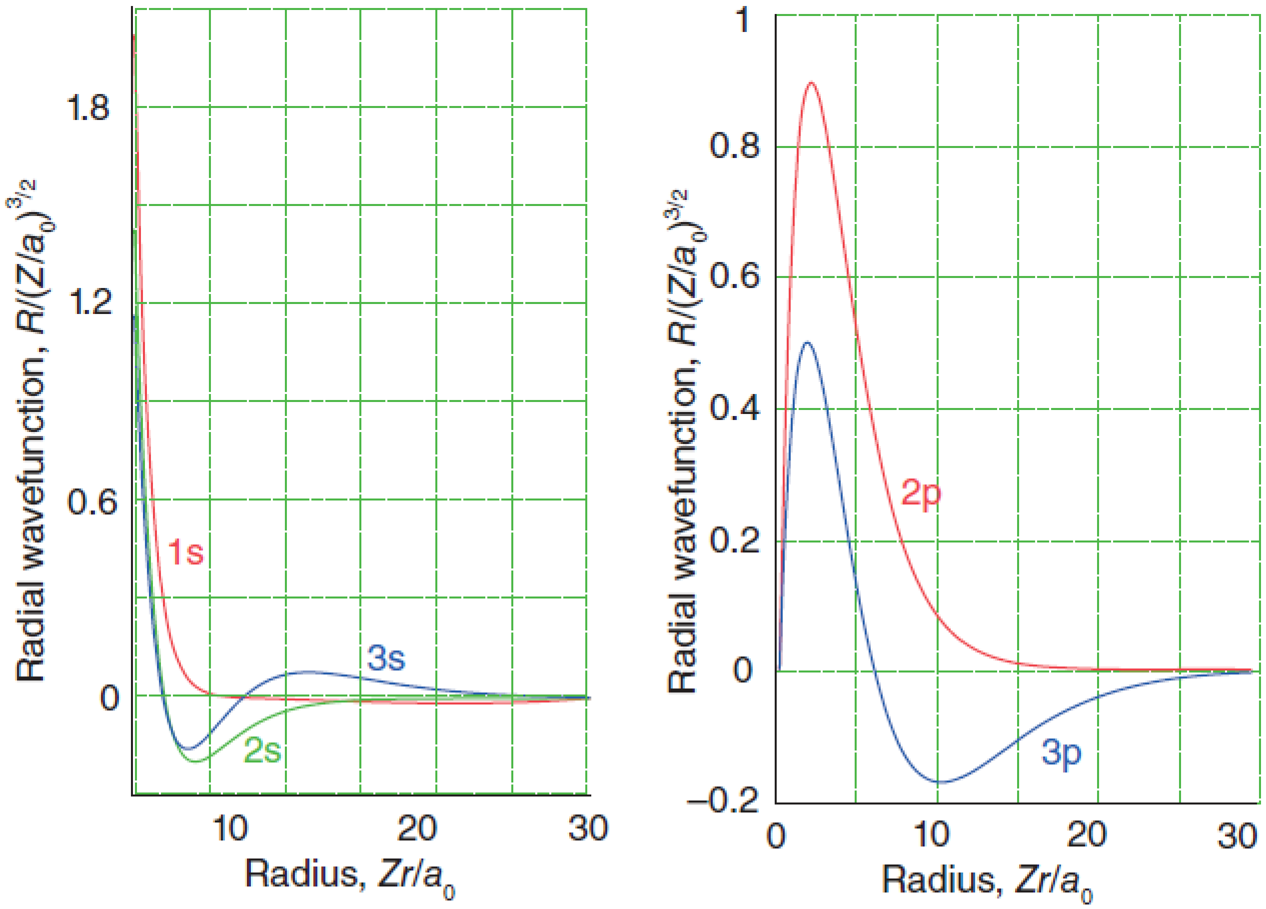


The Hydrogen-Like Wave Functions

Orbital Desig-nation	n	l	m_l	$R_{(r)}$	$\Theta_{(\theta)}\Phi_{(\phi)}$
1s	1	0	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-q}$	$\left(\frac{1}{4\pi}\right)^{1/2}$
2s	2	0	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-q)e^{-q/2}$	$\left(\frac{1}{4\pi}\right)^{1/2}$
2p_z	2	1	0	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} qe^{-q/2}$	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
2p_x	2	1	0	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} qe^{-q/2}$	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
2p_y	2	1	-1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} qe^{-q/2}$	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
3s	3	0	0	$\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18q+2q^2)e^{-q/3}$	$\left(\frac{1}{4\pi}\right)^{1/2}$

q = Zr/a

- The number of such spherical nodal surfaces arising from a radial function are $n - l - 1$
- For 1s orbital, the wavefunction with $n = 1$, $l = 0$ and number of radial node is 0, never passes through zero
- In 2s orbital, $n = 2$, $l = 0$, which passes through zero once and hence has one radial node.
- A 3s orbital passes through zero twice and so has two radial nodes.
- A 2p orbital ($n = 2$, $l = 1$) has no radial node because its radial wavefunction does not pass through zero anywhere
- For any series of orbital of the same type, the first occurrence has no radial node, the second has one radial node, and so on.

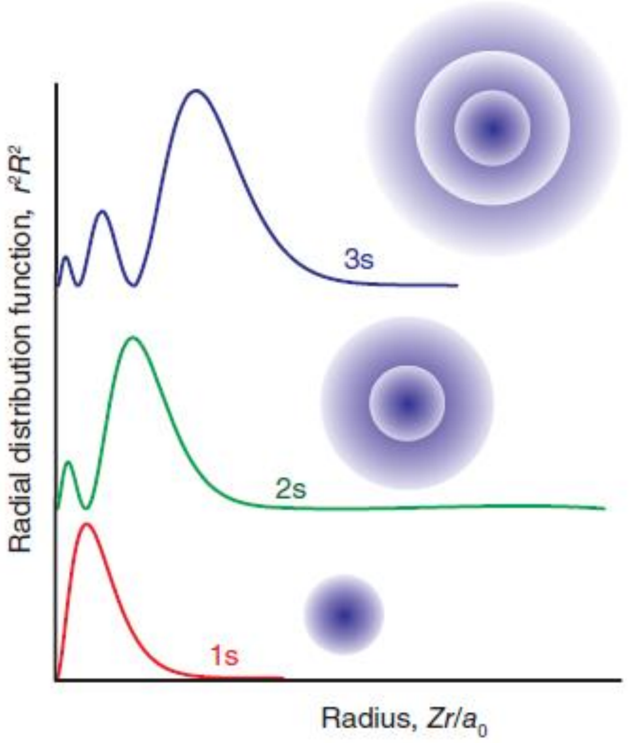


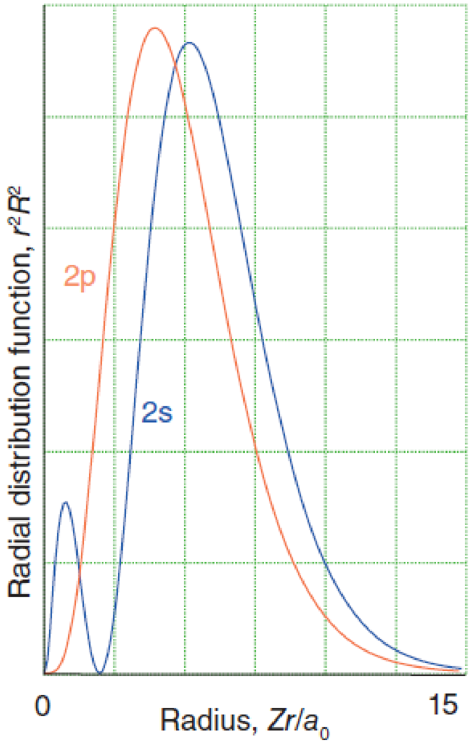
Radial wavefunctions of the 1s, 2s, 3s, 2p and 3p hydrogenic orbitals [nonzero amplitude at the nucleus (at $r = 0$)]

Radial distribution function

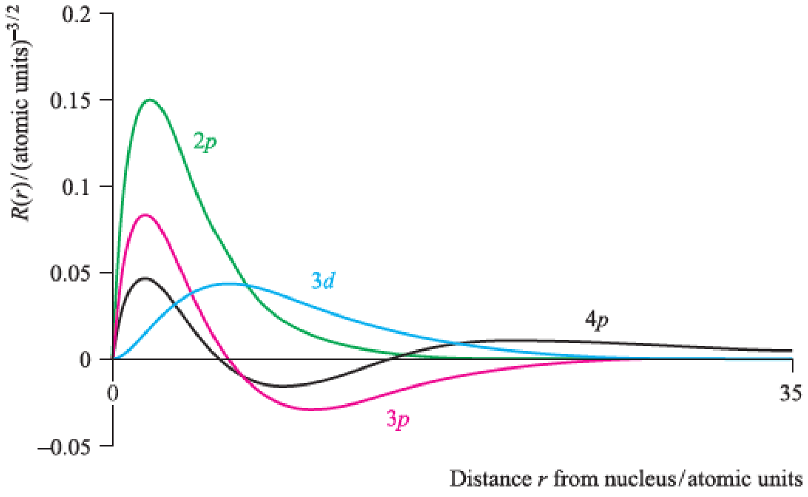
- Radial function $R(r)_{n,l}$ has no physical significance, but its square $R^2(r)_{n,l}$ is the probability of finding the electron in a small volume dv near the point at which $R(r)_{n,l}$ is measured
- For a given value of r the number of small volumes is $4\pi r^2$, so the probability of the electron being at a distance r from the nucleus is $4\pi r^2R^2(r)_{n,l}$. This is called radial distribution function.
- A radial distribution function gives the probability that an electron will be found at a given distance from the nucleus, regardless of the direction
- Regions where wavefunctions pass through zero are called nodes.
- There are two types of nodes. Radial nodes occur where the radial component of the wavefunction passes through zero and angular nodes occur where the angular component of the wavefunction passes through zero.
- The numbers of both types of node increase with increasing energy
- The plot of the radial distribution function ($4\pi r^2R^2(r)_{n,l}$) against r for various orbital in hydrogen atom are shown

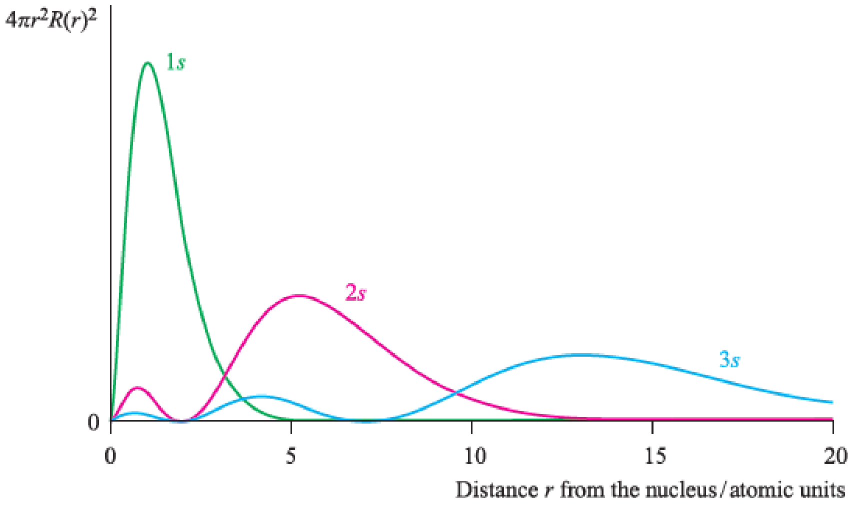
- For 1s orbital, Probability density at the nucleus is 0, because r =0. Resultant plot passes through maximum at an intermediate value of r, most probable distance
- Higher s-orbitals show nodes corresponding to the nodes in radial function
- Radial distribution function is always positive
- 2s orbital shows a inner maxima followed by a node and finally an outer maxima (two concentric lobes separated by a nodal surface)
- Probability maxima shift to right as n increases (2s moves away from the nucleus, compared to 1s)
- Small hump indicates that there is still some probability near the nucleus
- For a given value of n, the mean radius decreases as l increases (2p orbital has smaller mean than 2s)



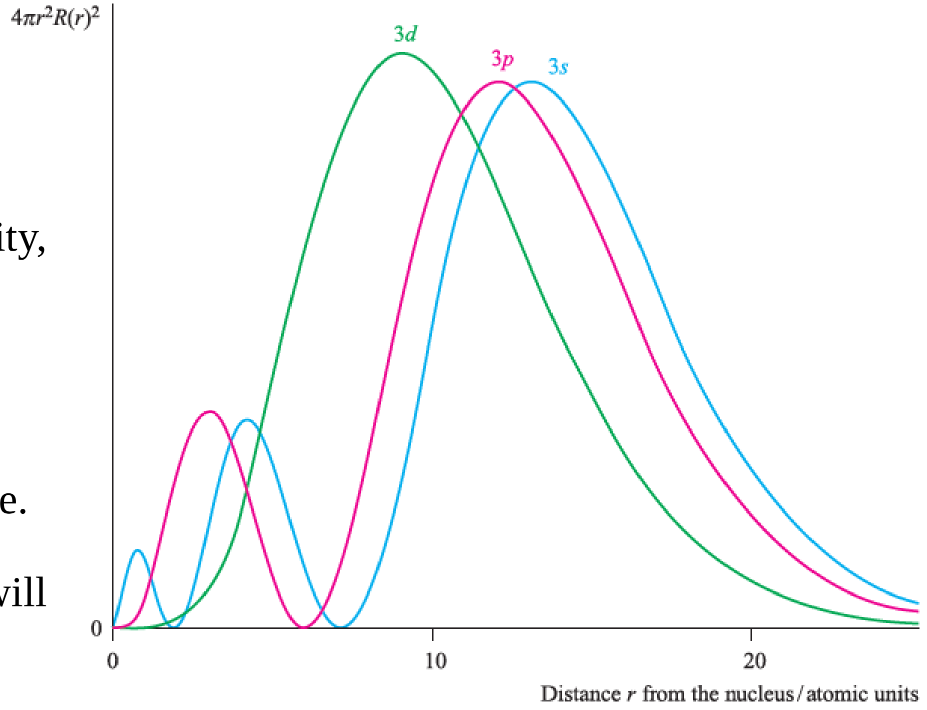


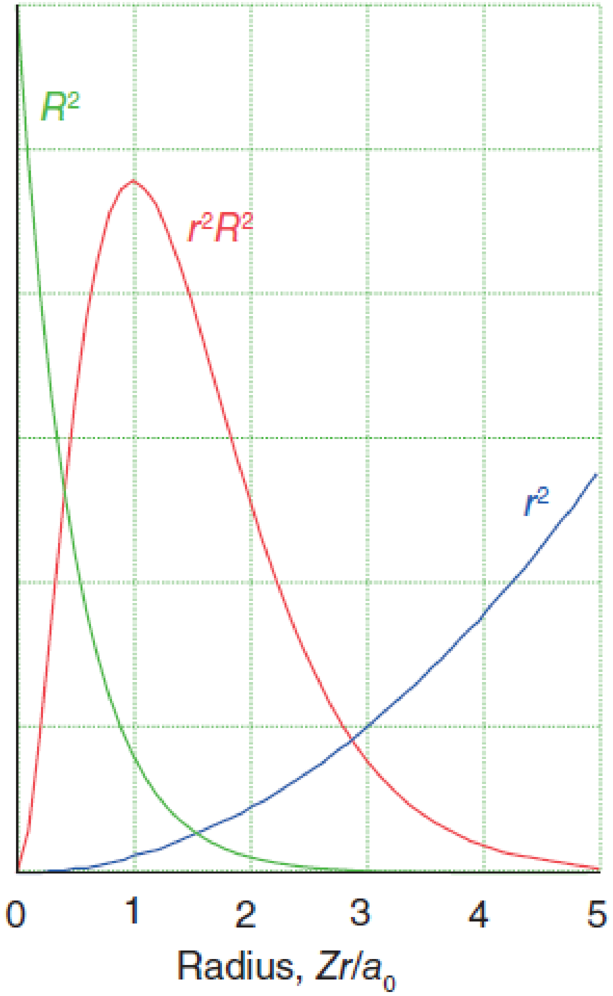
Radial distribution functions of hydrogenic orbitals. Although 2p orbital is *on average* closer to the nucleus, the 2s orbital has a high probability of being close to the nucleus on account of the inner maximum.





- Probability is zero at the nucleus (as r =0)
- Most probable distance increases considerably as *n* increases.
- Most probable radius decreases slightly as *l* increases.
- s-orbitals (except 1s) have shell like structure (concentric layers of electron density, onion like).
- Similarly, all except 2p and 3d orbitals have a shell structure.
- Outer orbital does not get full screening by the inner electrons from the nuclear charge.
- Since the 2s orbital penetrates somewhat into the core of 1s electrons, the screening will be less





- Radial distribution function, r^2R^2, of a hydrogenic 1s orbital.
- r^2R^2 is the product of r^2 (which increases as r increases) and the square of the radial component of the wavefunction ψ (labelled R^2 in the figure and which decreases exponentially).
- This distance increases as nuclear charge increases and passes through a maximum at $r = a_O/Z$.

Q. How many radial nodes do 3p, 3d, and 4f orbitals each have?

Answer: Number of radial nodes is given by the expression $n - l - 1$. The 3p orbitals have $n = 3$ and $l = 1$ and the number of radial nodes is $n - l - 1 = 1$. The 3d orbitals have $n = 3$ and $l = 2$. Therefore, the number of radial nodes is $n - l - 1 = 0$. The 4f orbitals have $n = 4$ and $l = 3$ and the number of radial nodes is $n - l - 1 = 0$. The 3d and 4f orbitals are the first occurrence of the d and f orbitals so this also indicates that they will have no radial node.

Self-test 1.3 How many radial nodes does a 5s orbital have?

Q. Which orbital gives the electron a greater probability of close approach to the nucleus in between for 2s and 2p hydrogenic orbitals?

*Answer: T*he radial distribution function of a 2p orbital approaches zero near the nucleus faster than a 2s electron does. This difference is a consequence of the fact that a 2p orbital has zero amplitude at the nucleus on account of its orbital angular momentum. The 2s electron has a greater probability of close approach to the nucleus, indicated by the inner maximum.

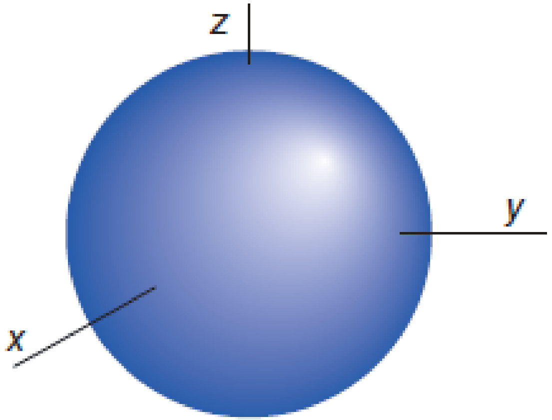
Self-test 1.4 Which orbital, 3p or 3d, gives an electron a greater probability of being found close to the nucleus?

Angular wave dependence of the wave function

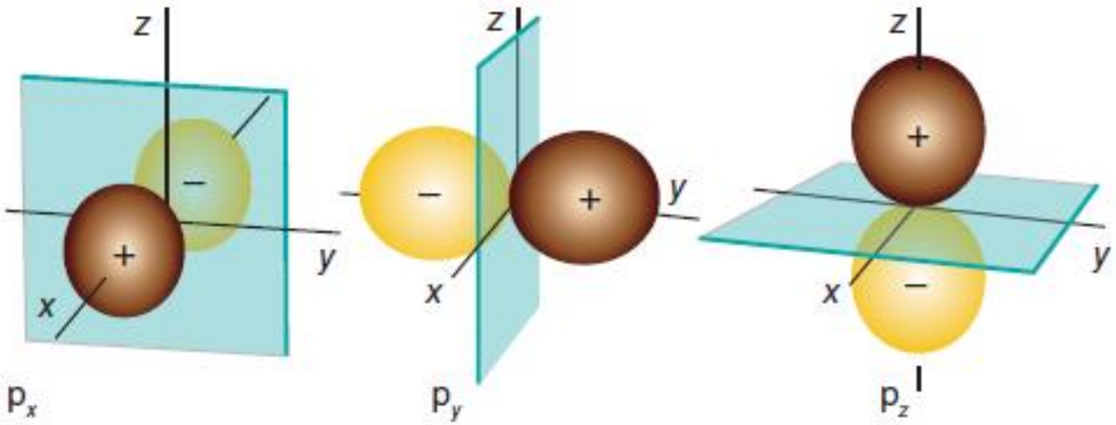
- The wave functions for single electron as obtained are often termed as atomic orbitals
- The shapes of these orbitals depend on the angles θ and ϕ or the spatial distribution of the orbitals
- The angular dependence is represented by spherical polar coordinates θ and ϕ given as $\Theta(\theta).\Phi(\phi)$ term
- The angular wavefunction expresses the variation of angle around the nucleus and describes the orbital's angular shape.
- The angular wavefunction, $Y(\theta, \phi)_{l,m}$ depends only on the direction, and is independent of distance from the nucleus (r).
- $Y^2(\theta, \phi)_{l,m}$ is the probability of finding an electron at a given direction θ and ϕ at any distance from the nucleus to infinity.
- The boundary surface of an orbital indicates the region of space within which the electron is most likely to be found
- The planes on which the angular wavefunction passes through zero are called angular nodes or nodal planes.
- An electron will not be found anywhere on a nodal plane.
- A nodal plane cuts through the nucleus and separates the regions of positive and negative sign of the wavefunction.
- An orbital with the quantum number *l* has *l* nodal planes.

Shapes of atomic orbitals

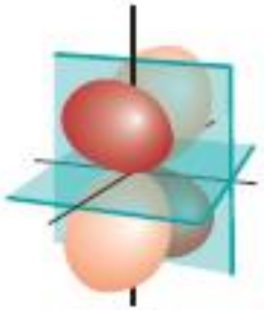
- An s orbital has the same amplitude at a given distance from the nucleus irrespective of the angular coordinates, spherically symmetrical.
- The surface is called the boundary surface of the orbital, high probability of finding the electron.
- s-orbital has *l* = 0, so has no node and the boundary surface of the orbital is spherical
- For s-orbital angular wave function $1/\sqrt{(4\pi)}$; thus s-orbital is independent of the angles θ and ϕ.
- Whatever be the values of θ and ϕ, the angular portion of the wavefunction is constant (hence spherical)

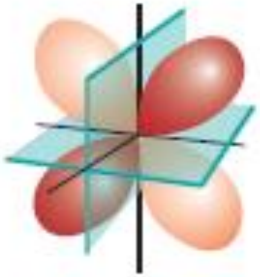


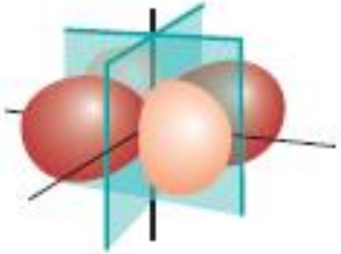
- Each p orbital, with $l = 1$, has a single nodal plane passing through the nucleus.
- Two lobes of the p-orbitals are shaded differently or labelled '+ (positive amplitude)' and '− (negative amplitude)'
- The boundary surfaces of the three p orbitals of a given shell are identical apart from their axes
- All orbitals with $l > 0$ have amplitudes that vary with angle and m_l values of +l, 0, or −l
- The orientation of p-orbitals can be calculated by considering the magnitudes and signs of trigonometric functions
- For p_z orbital, the $\Theta(\theta).\Phi(\phi)$ term contains $\cos\theta$ (directed along z-direction)
- The wave function for p_y orbital contains $\sin\theta\sin\phi$ term, hence corresponds to maximum electron density along y-direction
- The wave function for p_x orbital contains $\sin\theta\cos\phi$ term, indicates that the orbital points to the x-direction

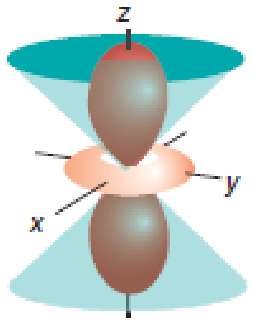


- Each d orbital, with $l = 2$, has two nodal plane passing through the nucleus.
- There are six possible combinations of double dumb-bell shaped orbitals around three axes: three with lobes between the axes and three with lobes along the axes. *But only five d orbitals are allowed.*
- Three in between the axes (d_{xy}, d_{yz}, d_{zx}). Two along the axes, one is assigned d_{x2-y2} (along the x and y axes) and other one is $d_{2z2-x2-y2}$ can be regarded as the superposition of two contributions viz. one with lobes along the z- and x-axes and the other with lobes along the z- and y-axes: simplified to d_{z2}
- Four of the orbitals have two perpendicular nodal planes that intersect in a line passing through the nucleus.
- The d_{z2} orbital looks different, the nodal surface forms two cones that meet at the nucleus.

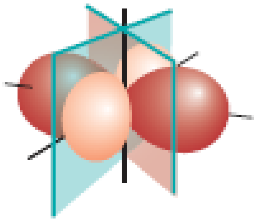

d_{zx}


d_{yz}

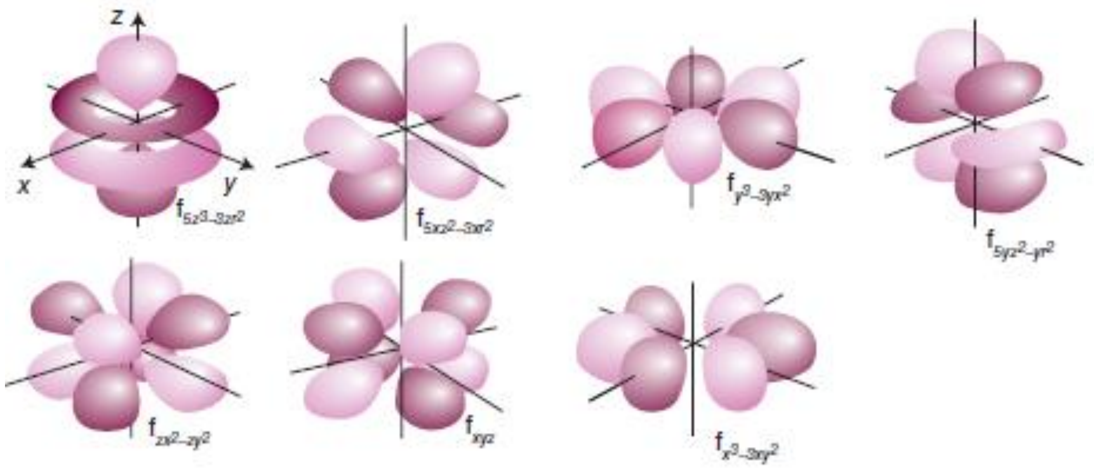

d_{xy}



d_{z^2}

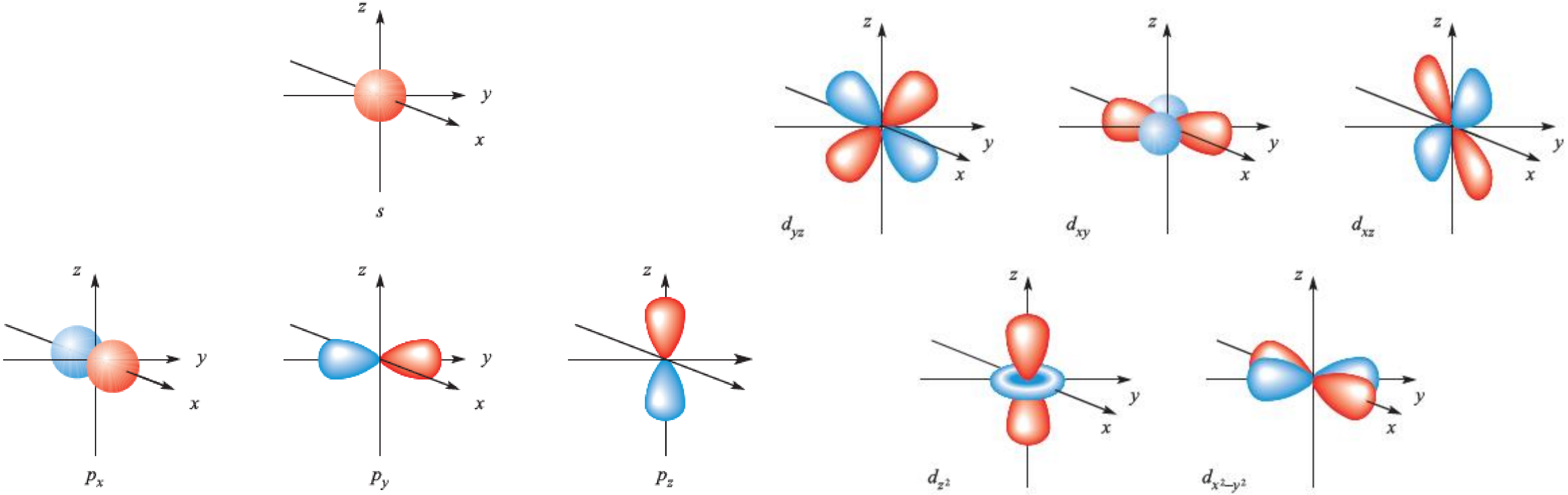

$d_{x^2-y^2}$

- Each f orbital, with *l* = 3, has three nodal plane passing through the nucleus.

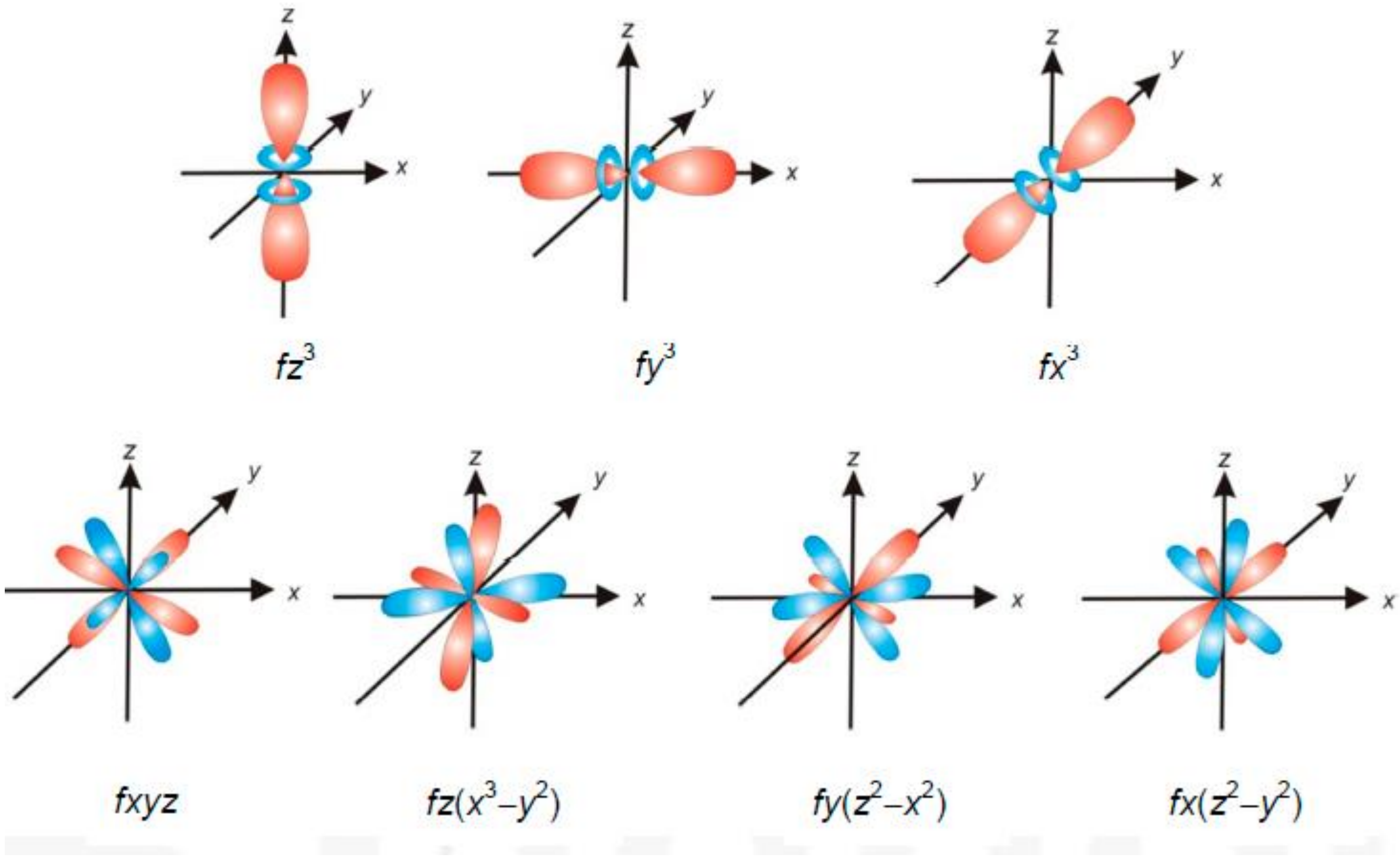


- For bonding, like signs must overlap (+ and – sign refer to symmetry wave function).
- Similarly 2s and 3s orbitals are spherically symmetrical because they do not involve θ and ϕ terms
- Likewise, the directional characteristics of 3p and 3d orbitals can also be interpretated
- A full representation of the probability of finding an electron requires the total wavefunction squared and includes both radial and angular probability squared
- The squaring of the total wave function does not change the shape of s-orbital but elongates the lobes of p-orbitals (no + and – sign as it is square of wave function)

Simplified form



Representations of an s, a set of three degenerate p and a set of five degenerate d atomic orbitals

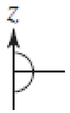
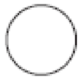
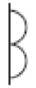
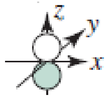
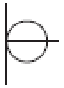
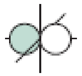
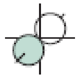
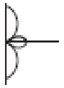
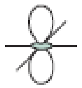
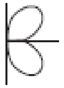
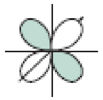
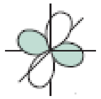
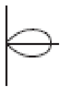
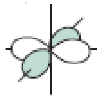
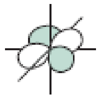


Representations of a set of seven degenerate f atomic orbitals

TABLE 2.4 Hydrogen Atom Wave Functions: Radial Functions

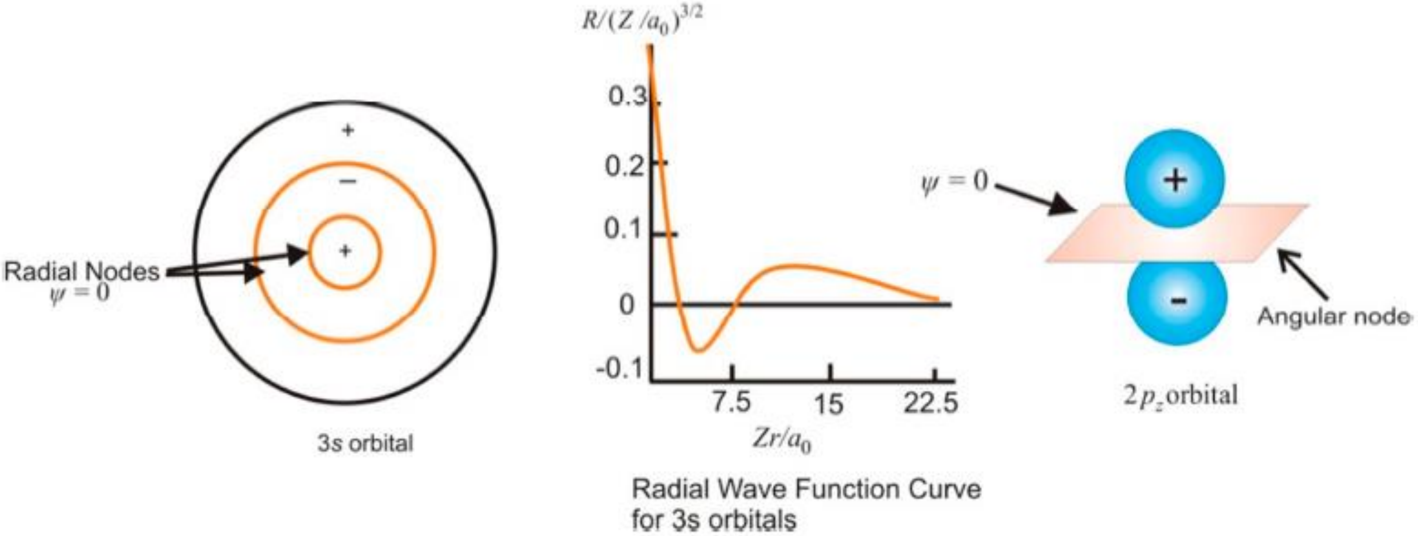
Radial Functions $R(r)$, with $\sigma = Zr/a_0$			
Orbital	n	l	$R(r)$
$1s$	1	0	$R_{1s} = 2\left[\frac{Z}{a_0}\right]^{3/2} e^{-\sigma}$
$2s$	2	0	$R_{2s} = 2\left[\frac{Z}{2a_0}\right]^{3/2} (2 - \sigma)e^{-\sigma/2}$
$2p$		1	$R_{2p} = \frac{1}{\sqrt{3}}\left[\frac{Z}{2a_0}\right]^{3/2} \sigma e^{-\sigma/2}$
$3s$	3	0	$R_{3s} = \frac{2}{27}\left[\frac{Z}{3a_0}\right]^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
$3p$		1	$R_{3p} = \frac{1}{81\sqrt{3}}\left[\frac{2Z}{a_0}\right]^{3/2} (6 - \sigma)\sigma\, e^{-\sigma/3}$
$3d$		2	$R_{3d} = \frac{1}{81\sqrt{15}}\left[\frac{2Z}{a_0}\right]^{3/2} \sigma^2 e^{-\sigma/3}$

TABLE 2.3 Hydrogen Atom Wave Functions: Angular Functions

Angular Factors					Real Wave Functions			
Related to Angular Momentum				Functions of θ	In Polar Coordinates	In Cartesian Coordinates	Shapes	Label
l	m_l	Φ	Θ		$\Theta\Phi(\theta, \phi)$	$\Theta\Phi(x, y, z)$		
$0(s)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$		$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{2\sqrt{\pi}}$		s
$1(p)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$		p_z
	$+1$	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{x}{r}$		p_x
	-1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{y}{r}$		p_y
$2(d)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2}\sqrt{\frac{5}{2}}(3\cos^2\theta-1)$		$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta-1)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{(2z^2-x^2-y^2)}{r^2}$		d_{z^2}
	$+1$	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$		d_{xz}
	-1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{yz}{r^2}$		d_{yz}
	$+2$	$\frac{1}{\sqrt{2\pi}}e^{2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{(x^2-y^2)}{r^2}$		$d_{x^2-y^2}$
	-2	$\frac{1}{\sqrt{2\pi}}e^{-2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{xy}{r^2}$		d_{xy}

Radial and Angular nodes and their significance

- Radial distribution function represents the electron density as a function of the distance from the nucleus
- Angular parts of wave function shows the electron distribution density
- Nodes can be radial and angular
- A radial node has a spherical surface with zero probability of having the electron density in that area
- Angular nodes are the nodal planes having zero electron density
- Sign of the symmetry of the wavefunction changes on moving from region to other across the nodal plane

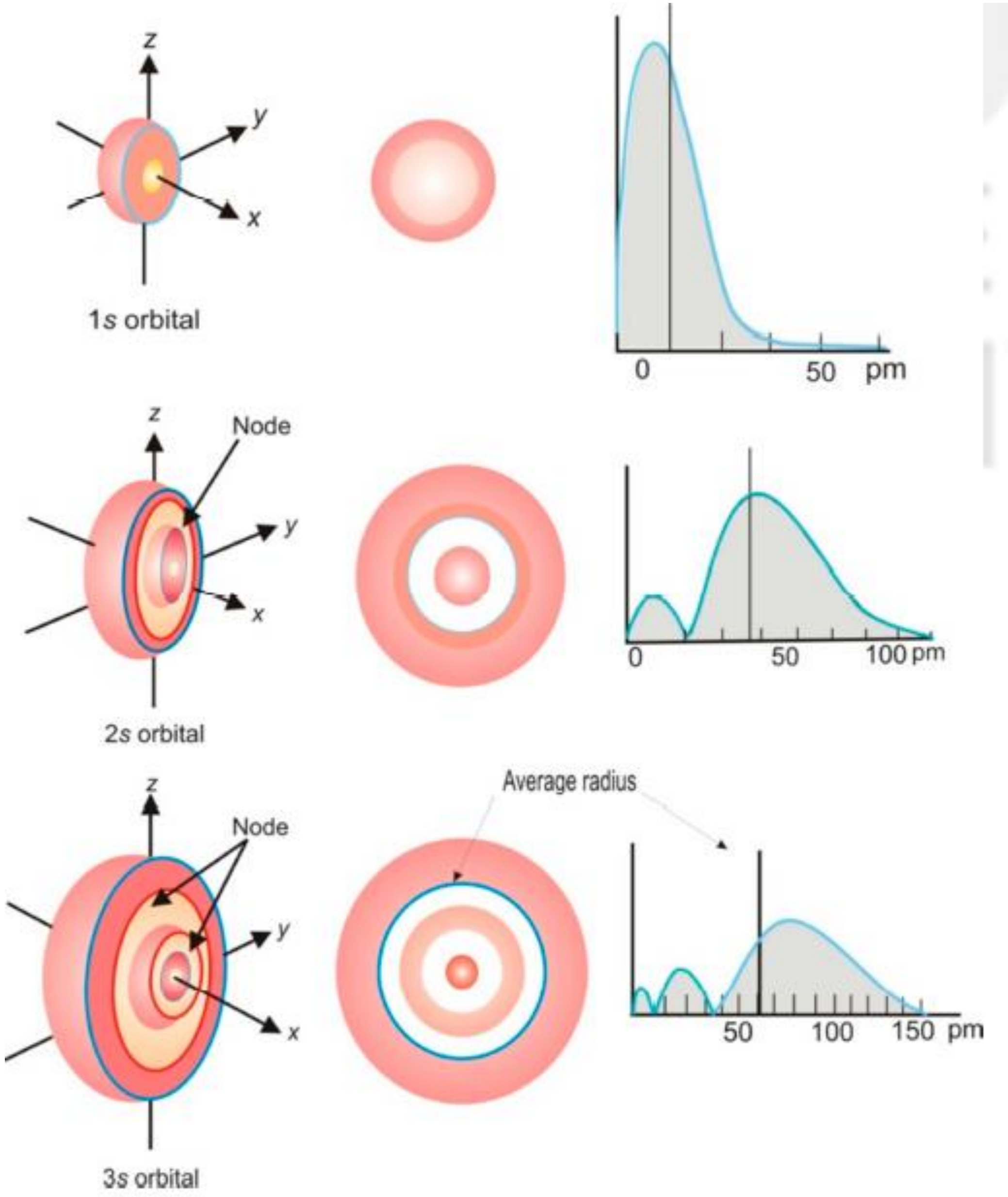


3s orbital

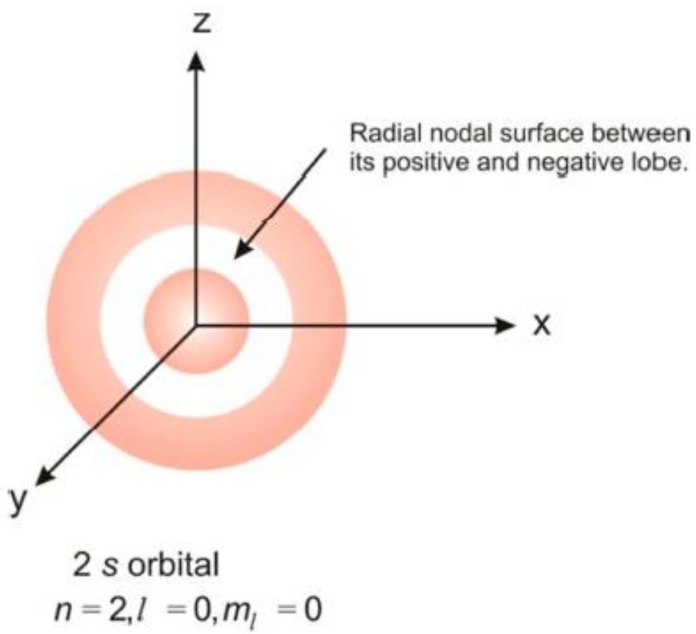
Radial Wave Function Curve for 3s orbitals

$2p_z$ orbital

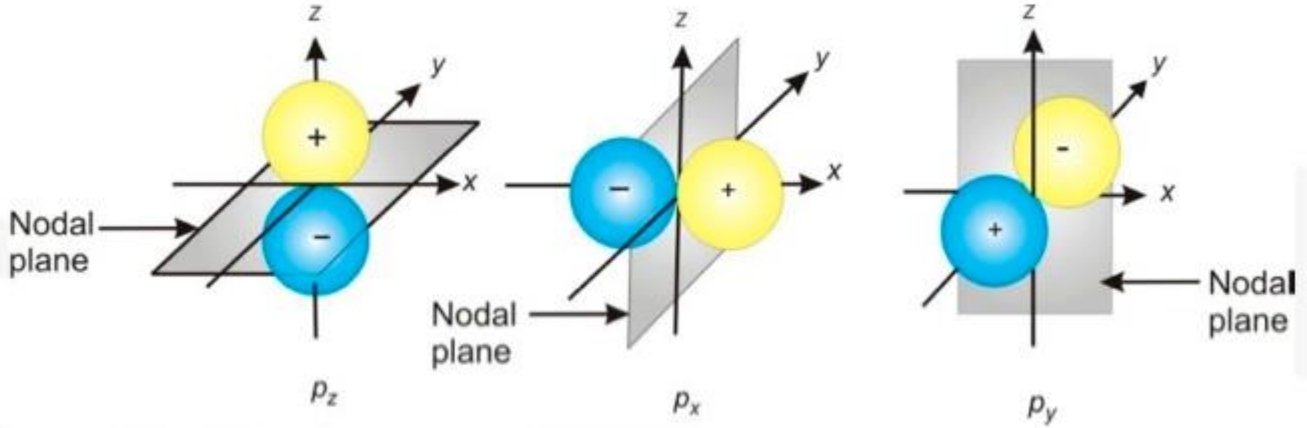
Radial and angular nodes in wave function.



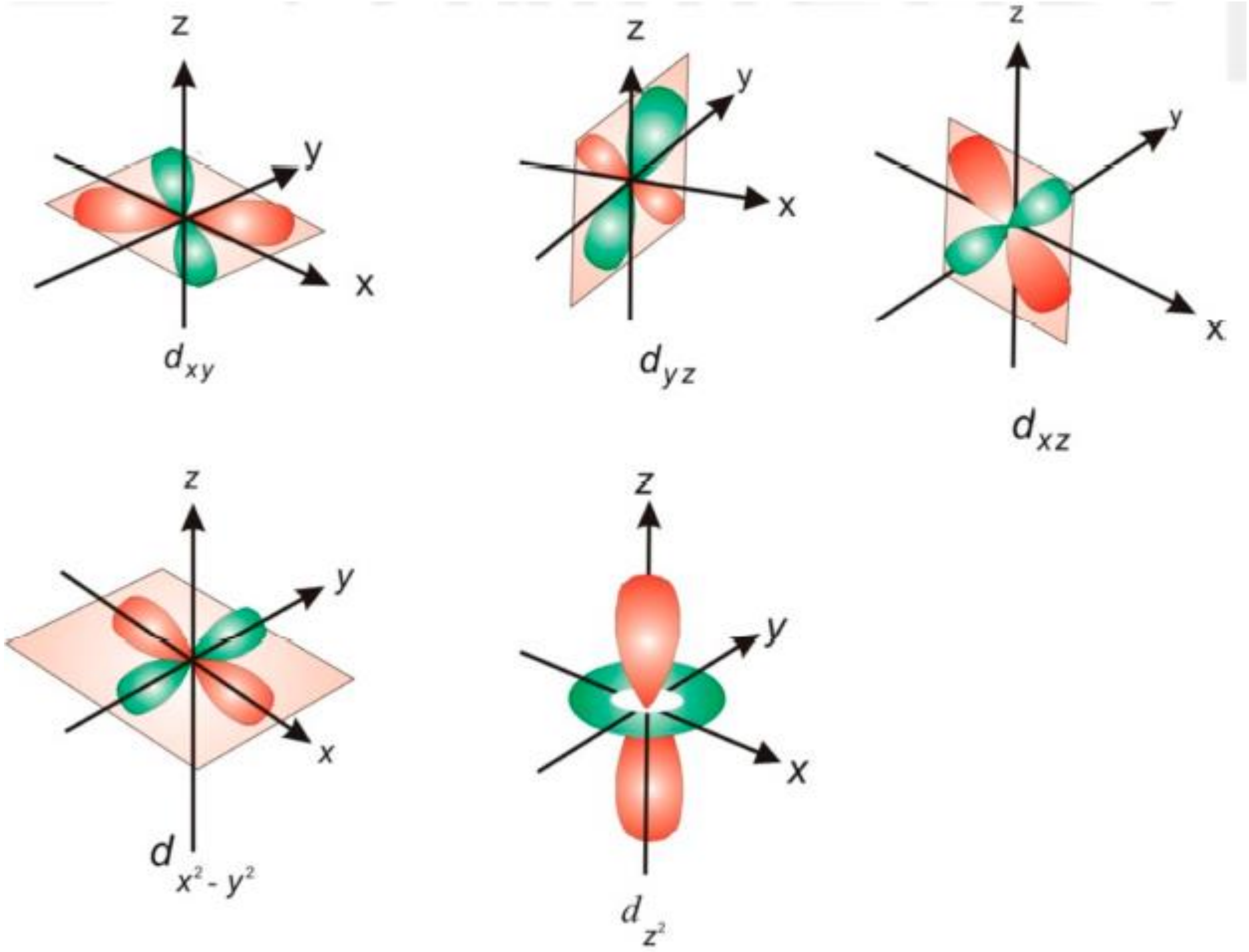
Radial nodes and radial probability density curves.



Radial node in the 2*s* orbital.



Nodal planes in *p* orbitals.



Nodal planes in *d* orbitals showing change of sign of symmetry.