

## **Lecture 9 :Title : Interpretation of wavefunction and modification for Alkali atoms**

Page-1

### **Objectives**

In this lecture

⇒ Born interpretation of the wavefunction is discussed

⇒ Radial probabilities of finding the electron in different orbit of hydrogen atom are elaborated

⇒ The angular part of the wavefunction for different orbital is shown

⇒ The departure in the spectra of alkali atom from hydrogen such as lithium, sodium is emphasized in the next lecture

⇒ The wavefunction calculated for the hydrogen atom in the previous lecture is complex quantity (includes  $e^{\pm im_l \Phi}$ ).

⇒ This can not be measured by any actual physical instrument. However, it contains all the information which the uncertainty principle allows us to know about the associated electrons.

⇒ The connection between the properties of the wavefunction  $\Psi(x,t)$  and the behavior of the electron is expressed in terms of the probability density  $P(x,t)$

⇒  $P(x,t)$  is the probability per unit length of finding the particle near the coordinate  $x$  at time  $t$ .

⇒ According to Max Born, 1962, the probability density  $P(x,t) = \Psi^*(x,t)\Psi(x,t)$  where  $\Psi^*(x,t)$  represents the complex conjugate of  $\Psi(x,t)$

***Born interpretation of the wavefunction:***

If at any instant of time 't', a measurement is made to locate the electron with the wavefunction  $\Psi(x,t)$ , the probability  $P(x,t)dx$  of finding a particle at a position between  $x$  and  $x+dx$  is proportional to  $|\Psi(x,t)|^2 dx$ .

$$P(x,t) = \Psi^*(x,t)\Psi(x,t) = |\Psi(x,t)|^2 \quad \text{.....9.1}$$

It implies that sign of the wavefunction has no direct physical significance. In the figure-9.1, the wavefunction has changed its sign but the probability of finding the electron is symmetric with respect to the nucleus at  $r/a_0 = 0$

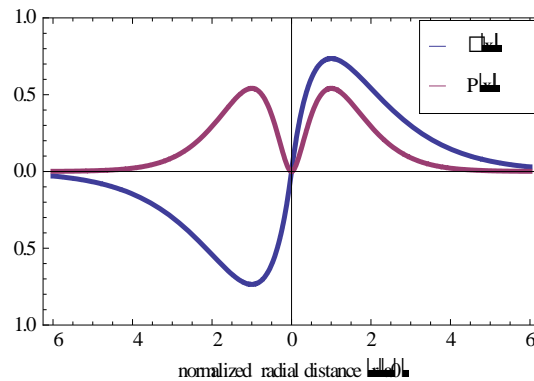
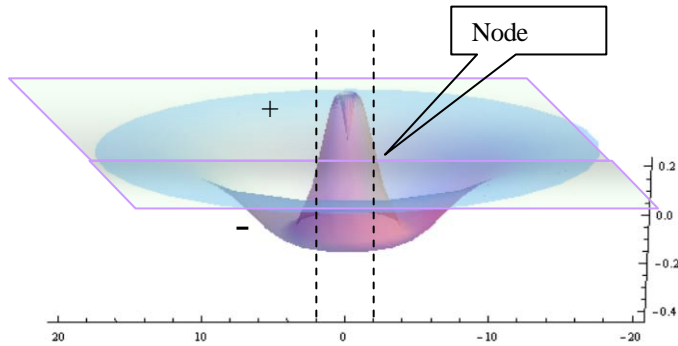


Figure-9.1

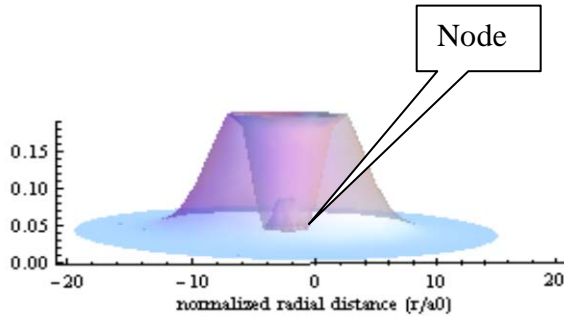
If the wavefunction changes sign as shown in the figure-9.2, it is called node ( $\Psi(x,t) = 0$ ). The probability of finding the electron (figure-9.3) at node is zero because

$$P(x,t) = \Psi^*(x,t)\Psi(x,t) = |\Psi(x,t)|^2 \quad \dots\dots 9.2$$



Wavefunction of the electron

Figure-9.2



Probability of finding the electron

Figure-9.3

In the previous lecture, we have evaluated the wavefunction of the electron in Hydrogen atom as

$$\Rightarrow \Psi_{n,\ell,m_\ell} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n\{(n+\ell)!\}^3}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right) \times \sqrt{\frac{(2\ell+1)(\ell-m_\ell)!}{4\pi(\ell+m_\ell)!}} P_\ell^{m_\ell}(\cos\theta) \quad \text{.....9.3}$$

$$\Rightarrow \Psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_l^{m_l}(\theta,\phi)$$

Where  $n \Rightarrow$  principal quantum number = 1, 2, 3, 4,....

$l \Rightarrow$  azimuthal quantum number = 0, 1, 2, .....,  $n-1$

and  $m_l \Rightarrow$  magnetic quantum number =  $-l, -l+1, \dots, -2, -1, 0, 1, 2, \dots, l+1=2l+1$  values

And the Energy  $E_n = -\frac{Z^2 \mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = \frac{-13.6 \text{ eV}}{n^2} = -\frac{R}{n^2} \quad \text{.....9.4}$

The energy depends only on  $n$ , but the functional form of  $R(r)$  depends on both  $n$  and  $l$ , and so we write the radial wavefunction as  $R_{n,l}(r)$  and angular part  $Y$  depends on  $l$  and  $m_l$ . Following table provides the energy and the nomenclature of the states.

Principal quantum no.	Orbital quantum no.	nomenclature	Magnetic quantum no.	Energy
$n = 1$ (K shell)	$l = 0$ (s subshell)	1s state	$m_l = 0$	-13.6 eV
$n = 2$ (L shell)	$l = 0$ (s subshell)	2s state	$m_l = 0$	-3.4 eV
		2p state	$m_l = -1$	
		2p state	$m_l = 0$	
		2p state	$m_l = 1$	
$n = 3$ (M shell)	$l = 0$ (s subshell)	3s state	$m_l = 0$	-1.51 eV
		3p state	$m_l = -1$	
		3p state	$m_l = 0$	
		3p state	$m_l = 1$	
	$l = 1$ (p subshell)	3d state	$m_l = -2$	
		3d state	$m_l = -1$	
		3d state	$m_l = 0$	
		3d state	$m_l = 1$	
	$l = 2$ (d subshell)	3d state	$m_l = 1$	
		3d state	$m_l = 2$	

In the following figure-9.4, we plot the radial functions  $R_{n,l}(r)$ , the reduced radial functions  $U_{n,l}(r) = r R_{n,l}(r)$ , and the radial probability densities  $P_{n,l}^{rad}(r) = (U_{n,l}(r))^2$  for different states of hydrogen atom. We will also see the plot for different orbitals of hydrogen atom.

***The first orbit  $n = 1, l = 0$  and  $m_l = 0$ , the K shell***

⇒ In this plot we can see the effect of the factor  $r$  in  $U_{1s}(r) = r R_{1s}(r)$ . Here,  $R_{1s}(r)$  goes to  $2/a_0$  (Bohr radius) at  $r = 0$ , while  $U_{1s}(r)$  goes to zero. The factor of  $r$  in  $U_{1s}(r)$  also introduces a *peak* at  $1/a_0$ .

⇒ There is no node for  $1s$  state.

⇒ The probability density  $P_{1s}^{rad}(r)$  goes to zero at  $r = 0$ , it means that the probability of finding the electron at the nucleus is zero.  $P_{1s}^{rad}(r)$  shows also a peak at  $1/a_0$  which is the same as Bohr radius and the peak value is 0.54.

⇒ *Conceptually, peaks in  $P_{n,l}^{rad}(r)$  are radii near which an electron in a state  $n, l, m_l$  is most likely to be found.*

⇒ Because of the gradual decay of  $P_{n,l}^{rad}(r)$  on the large- $r$  side of this peak, the calculated *mean radial position* turns out to be larger than the location of the peak

Following figure is the  $1s$  orbital

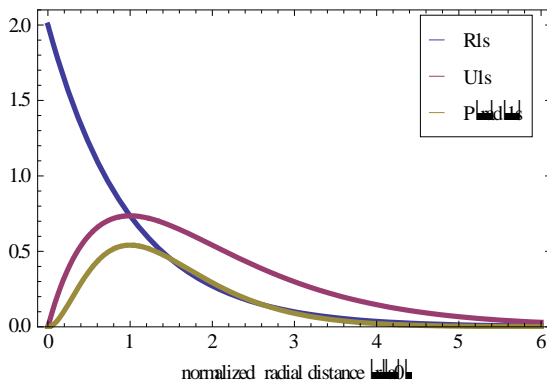
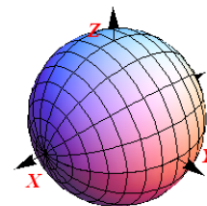


Figure-9.4



1s orbital

Figure-9.5

The second orbit  $n = 2$  ( L shell),  $l = 0, m_l = 0$  and  $l = 1, m_l = 0, \pm 1$

□

⇒ The  $2s$  radial function in the figure-9.6 decays as  $r \rightarrow \infty$  more gradually than  $U_{1s}(r)$ . Moreover, the  $2s$  radial probability density has *two peaks*: one at  $0.76 a_0$  and next one at  $5.24 a_0$ .

⇒ The height of the peak nearest the nucleus, 0.052, is much smaller than that of the outer peak, 0.19. The presence of a small peak in  $P_{2s}^{rad}(r)$  relatively near the origin is called *penetration*.

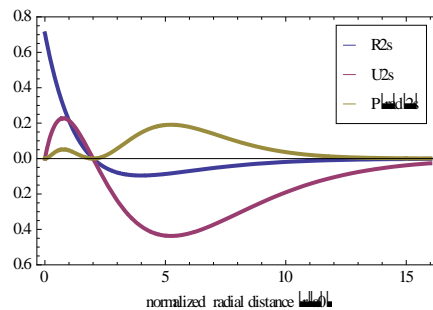
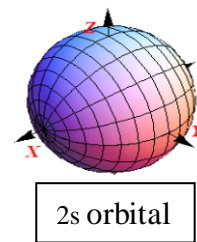


Figure-9.6



2s orbital

⇒ The  $2p$  functions in this figure-9.7 differ strikingly near the origin from the  $1s$  and  $2s$  functions. Because of the  $l = 1$  barrier term in the  $r$  radial equation,  $P_{2p}^{rad}(r)$  rises from zero.

⇒  $U_{2p}(r)$  has a classically forbidden region near the origin.

□

□

Following figures are three  $p_x, p_y$  and  $p_z$  orbitals.

□

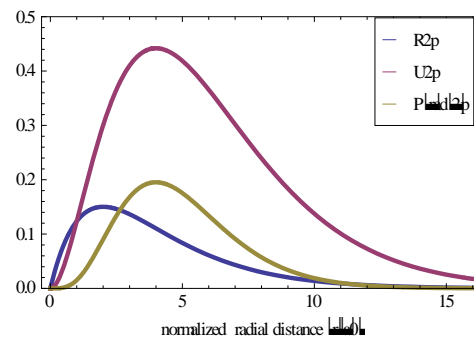
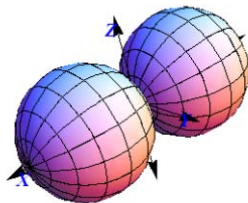
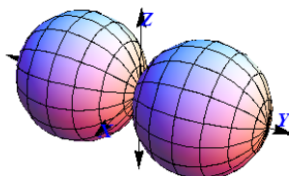


Figure-9.7

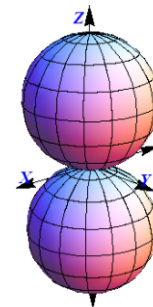


$p_x$  orbital



$p_y$  orbital

Figure-9.8



$p_z$  orbital

To compare the differences between the functions  $U_{n,l}(r) = r R_{n,l}(r)$  and  $P_{n,l}^{rad}(r) = (U_{n,l}(r))^2$  for the  $n = 1$  and  $n = 2$  states of hydrogen, they are plotted on the same graph as shown in the following figures-9.9 and 9.10.

⇒ The increase in  $l$  by 1 from  $2s$  to  $2p$  states means that neither  $U_{2p}(r)$  nor  $P_{2p}^{rad}(r)$  have nodes. Asymptotically, both functions decay at the same rate as their  $2s$  counterparts, because the decay constant for a pure- Coulomb potential energy doesn't depend on  $l$ .

⇒ The sole peak in  $P_{2p}^{rad}(r)$  occurs at  $r = 4 a_0$ , where its value is 0.19. Interestingly, the mean radius of  $2p$  state  $= 5 a_0$  is  $1a_0$  smaller than that of the  $2s$  state.

⇒ In the plots of reduced radial functions  $U_{1s}(r)$ ,  $U_{2s}(r)$  and  $U_{2p}(r)$ , note the differences in these functions rise from 0. The functions  $U_{1s}(r)$  and  $U_{2s}(r)$  rise like  $r$ , in which  $U_{1s}(r)$  is faster than  $U_{2s}(r)$  while  $U_{2p}(r)$  rises like  $r^2$ .

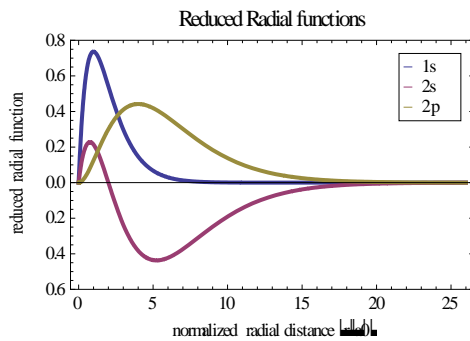


Figure-9.9

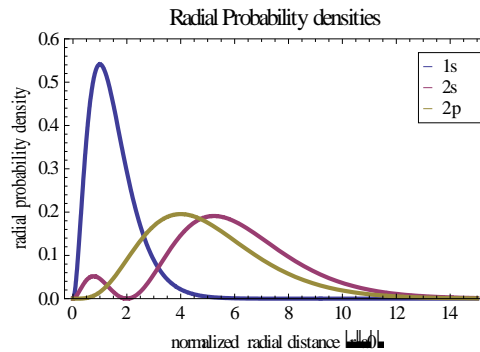


Figure-9.10

The third orbit  $n = 3$  ( M shell),  $l = 0, m_l = 0$  and  $l = 1, m_l = 0, \pm 1$  and  $l = 2, m_l = 0, \pm 1, \pm 2$

The general features are from the following graphs in figure-9.11:

$\Rightarrow U_{3s}(r)$  has two nodes,  $U_{3p}(r)$  has one, and  $U_{3d}(r)$  has none.

$\Rightarrow$  The  $3s$  radial probability density has *two* regions fairly near the origin where there is a *small but nonzero* chance of finding the electron.

$\Rightarrow$  The  $3s$  state is the most penetrating, because its radial function is unaffected by a barrier, while the  $3d$ , which suffers the strongest barrier, is the least penetrating.

$\Rightarrow$  Since the number of nodes  $= n - l - 1$  decreases with increasing  $l$ , small  $l$  radial functions have the most nodes.

$\Rightarrow$  Since these nodes are radii where the probability density is zero, radial probability densities for low-  $l$  are characterized by small regions of non-zero probability very near the nucleus.

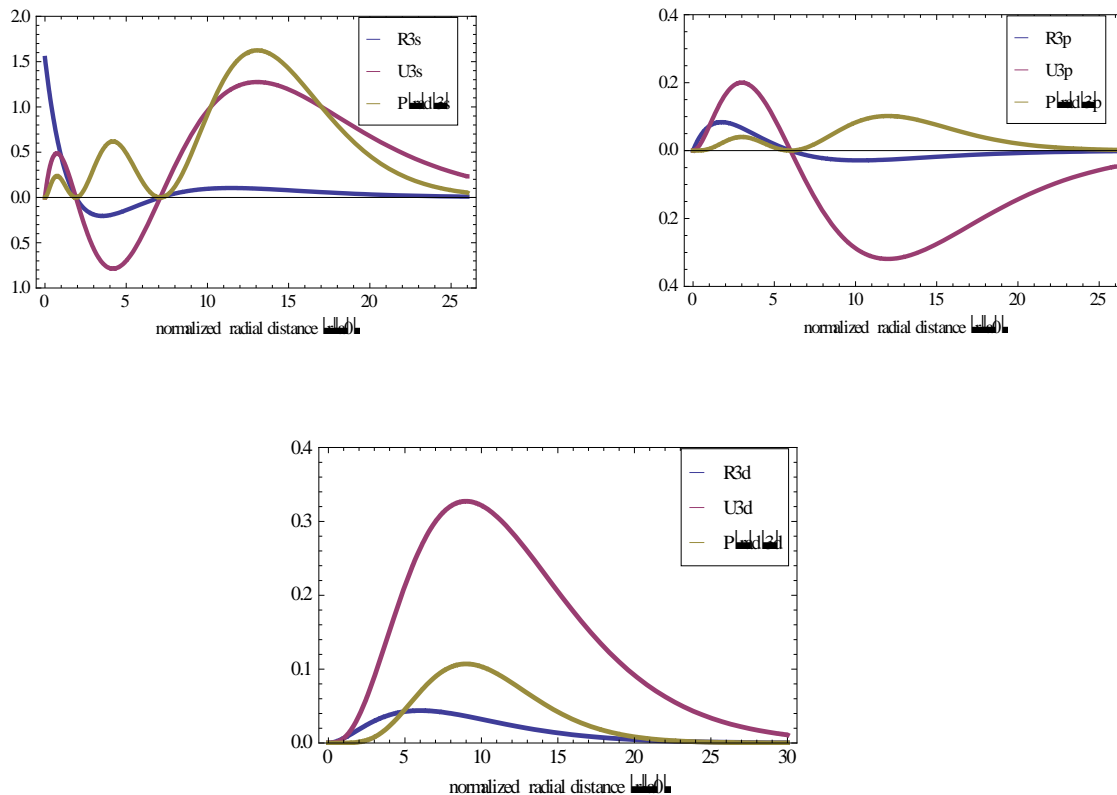


Figure-9.11

The following graphs in figure 9.12 show the comparison of reduced radial functions and probability densities of  $n = 3$  states

⇒ The  $n = 3$  states show that as  $l$  increases, the outermost peak moves inward, to smaller radial distance.

⇒ The magnitude of each peak increases as the radial distance increases. This increase occurs because as  $l$  increases by one unit, the probability density, which must remain normalized to unity, loses one inner peak.

⇒ In spite of all these variations, the energies of all these  $n = 3$  states is the same,  $E_3 = 1.51 \text{ eV}$ .

⇒ The range of  $r$  values required to plot all of the radial probability density for the  $n = 3$  states is more than twice for states with  $n < 3$ .

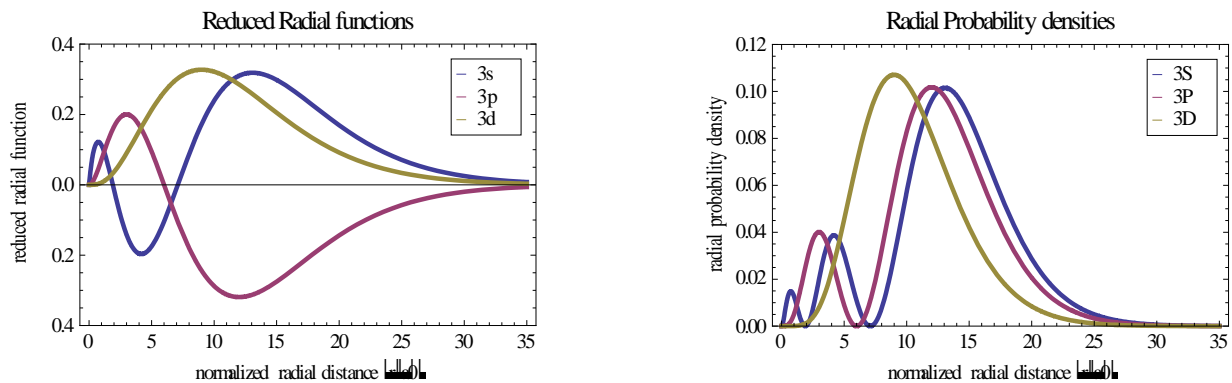
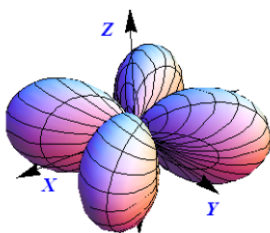
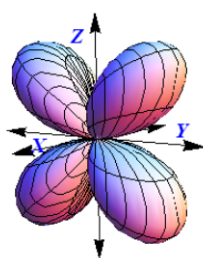


Figure-9.12

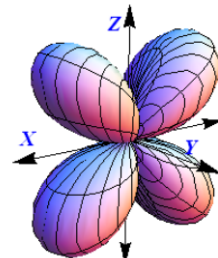
The five  $d$  – orbitals are shown in figure-9.13



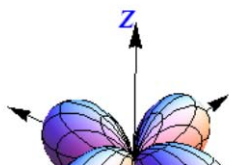
$d_{xy}$  orbital

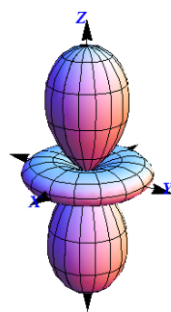


$d_{yz}$  orbital



$d_{xz}$  orbital





$d_{z^2}$  orbital

Figure-9.13

Following graphs in figure-9.14 show the comparison of the probability densities for  $n = 1, 2, 3, 4$  states.

⇒ All  $s$ -state radial probability densities for  $n = 1, 2, 3$ , and  $4$  behave the same way near the origin. None suffer the  $l$  barrier, so all have peaks near the origin.

⇒ Because the number of nodes in an  $s$  state function increases by one with each unit increase in  $n$ , the number of peaks also increases by one.

⇒ Only for the  $1s$  state has a large peak near the origin; the magnitudes of the near-origin peaks in radial probability density for  $n > 1$  decrease rapidly with increasing  $n$ .

⇒ Consequently the probability of finding the electron far from the nucleus increases appreciable as  $n$  increases.

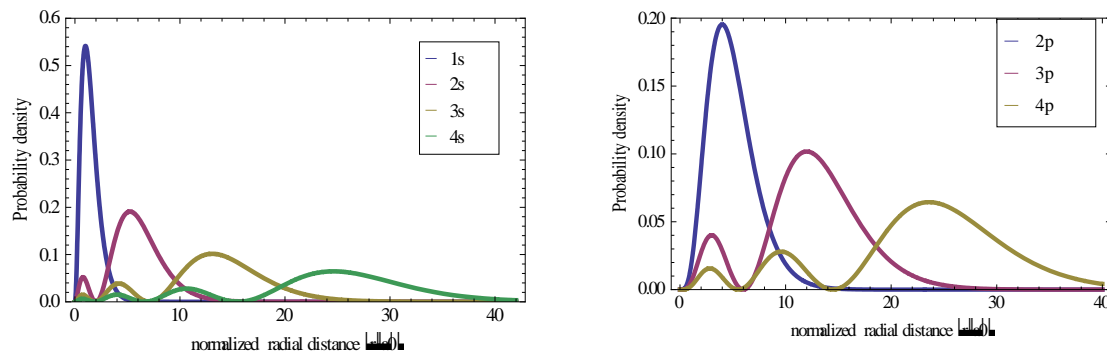


Figure-9.14

### Main features to remember

⇒  $l = 0$ ,  $s$ -states do not vanish at  $r = 0$ .

⇒  $l \neq 0$ , states vanish at  $r = 0$  and have their maximum probability amplitude further out with increasing  $l$ .

⇒ The size, position of peak probability, scales with  $\sim n^2$ .

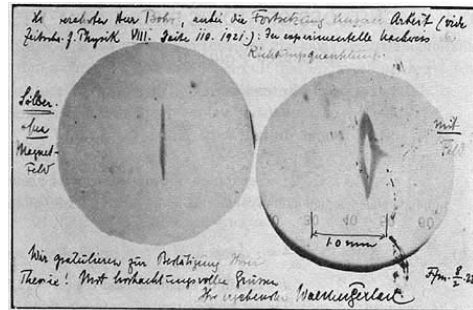
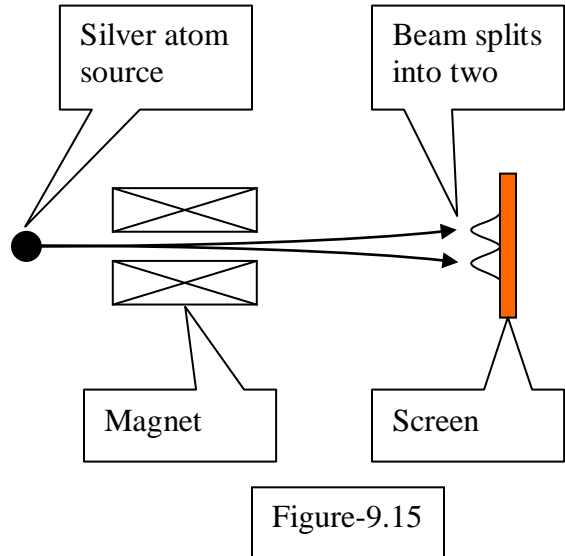
⇒ The  $l = 0$  function crosses the axis  $(n - 1)$  times i.e. it has  $(n - 1)$  nodes.

⇒  $l = 1$  has  $(n - 2)$  nodes and so on.

⇒ Maximum  $l = n - 1$  has no nodes (except at  $r = 0$ )

## Stern-Gerlach Experiment

In 1922, Stern and Gerlach launched a beam of Silver (Ag) atoms through a non-uniform magnetic field and detected them at a screen as shown in the figure-9.15.



Gerlach's postcard, dated 8 Feb, 1922, to Niels Bohr showing a photograph of the beam splitting,

⇒ Classical physics does not predict distinct spots. Distinct spots mean the magnetic moment is quantized.

⇒ This can not be due to orbital magnetic moment because orbital magnetic quantum number is odd, we would expect odd number of spots.

⇒ This marked the discovery of the electron spin. A new type of angular momentum, with a quantum number that can take on only *two* values:

$$s = \frac{1}{2}, \quad m_s = \pm \frac{1}{2}$$

This new kind of angular momentum is known as SPIN.

This spin sometimes visualize by the classical spin picture as shown in figure-9.16.

However, this “spinning” ball picture shown in figure-9.16 is not realistic, because it would require that the tiny electron be spinning so fast that parts would travel faster than  $c$ .

So the spin is another type of angular momentum.

**So, we need FOUR quantum numbers to specify the electronic state of a hydrogen atom**

**$n, l, m_l, m_s$  (where  $m_s = -1/2$  and  $+1/2$ )**

**Page-13**

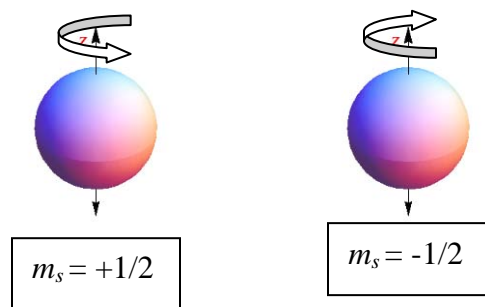


Figure-9.16

## Recap

In this lecture, we have learnt

⇒ Born interpretation of the wavefunction is that the wavefunction has no direct physical significance, only the probability of finding the electron is important.

⇒ Radial probabilities of finding the electron in different orbit of hydrogen atom are different, *s* orbits is the most penetrating.

⇒ Electron in an atom can be designated by **FOUR quantum numbers.**

⇒  **$n, l, m_l, m_s$**  (where  $m_s = -1/2$  and  $+1/2$ )