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 $e^{\pm i n\Phi}$).

⇒ 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 \(|\Psi(x,t)|^2\ dx\).

\[
P(x,t) = \Psi^*(x,t)\Psi(x,t) = |\Psi(x,t)|^2
\]

\[
\text{Figure-9.1}
\]

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 \(r/a_0 = 0\)
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
\[ P(x,t) = \Psi^*(x,t)\Psi(x,t) = |\Psi(x,t)|^2 \]  
\[ \ldots 9.2 \]
In the previous lecture, we have evaluated the wavefunction of the electron in Hydrogen atom as

\[ \Psi_{n,l,m_l} = \frac{2^{l+1}}{(n a_0)^{3/2}} \left( \frac{n-l-1}{n} \right) e^{-r/n a_0} \frac{2r}{n a_0} L_{n-l-1} \left( \frac{2r}{n a_0} \right) \times \frac{(2l+1)(-m_l)!}{4\pi (l+m_l)!} P_{\ell}^{m_l} (\cos \theta) \]

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 = \(-l, -l+1, \ldots, -1, 0, 1, \ldots, l\) values

And the Energy \( E_n = -\frac{Z^2 \mu e^4}{(4\pi \varepsilon_0)^2} \frac{1}{2\hbar^2 n^2} = -\frac{13.6 \text{ eV}}{n^2} = -\frac{R}{n^2} \)

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.

<table>
<thead>
<tr>
<th>Principal quantum no.</th>
<th>Orbital quantum no.</th>
<th>nomenclature</th>
<th>Magnetic quantum no.</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 1 ) (K shell)</td>
<td>( l = 0 ) (s subshell)</td>
<td>1s state</td>
<td>( m_l = 0 )</td>
<td>-13.6 eV</td>
</tr>
<tr>
<td>( n = 2 ) (L shell)</td>
<td>( l = 0 ) (s subshell)</td>
<td>2s state</td>
<td>( m_l = 0 )</td>
<td>-3.4 eV</td>
</tr>
<tr>
<td></td>
<td>( l = 1 ) (p subshell)</td>
<td>2p state</td>
<td>( m_l = -1 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( l = 1 ) (p subshell)</td>
<td>2p state</td>
<td>( m_l = 0 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2p state</td>
<td>( m_l = 1 )</td>
<td></td>
</tr>
<tr>
<td>( n = 3 ) (M shell)</td>
<td>( l = 0 ) (s subshell)</td>
<td>3s state</td>
<td>( m_l = 0 )</td>
<td>-1.51 eV</td>
</tr>
<tr>
<td></td>
<td>( l = 1 ) (p subshell)</td>
<td>3p state</td>
<td>( m_l = -1 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( l = 1 ) (p subshell)</td>
<td>3p state</td>
<td>( m_l = 0 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3p state</td>
<td>( m_l = 1 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( l = 2 ) (d subshell)</td>
<td>3d state</td>
<td>( m_l = -2 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( l = 2 ) (d subshell)</td>
<td>3d state</td>
<td>( m_l = -1 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( l = 2 ) (d subshell)</td>
<td>3d state</td>
<td>( m_l = 0 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( l = 2 ) (d subshell)</td>
<td>3d state</td>
<td>( m_l = 1 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3d state</td>
<td>( m_l = 2 )</td>
<td></td>
</tr>
</tbody>
</table>
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 $P_{n,l}^{\text{rad}}(r) = (U_{n,l}(r))^2$ 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 $2a_0$ (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 $1a_0$.

⇒ There is no node for $1s$ state.

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

⇒ *Conceptually, peaks in $P_{n,l}^{\text{rad}}(r)$ 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 $P_{1s}^{\text{rad}}(r)$ 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

![1s orbital](image)
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 \( r \to \infty \) 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*.

⇒ 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.
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 1$a_0$ 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](image1.png) ![Figure-9.10](image2.png)
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:

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

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

⇒ 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.

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

⇒ 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.

\[ \text{Figure-9.11} \]
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, looses one inner peak.

⇒ In spite of all these variations, the energies of all these $n = 3$ states is the same, $E_3 = 1.51$ 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 $n < 3$.

The five $d$ – orbitals are shown in figure 9.13.
Figure 9.13

$d_{z^2}$ orbital
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 $n = 1, 2, 3, 4$ 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.

![Graphs showing probability densities for $n = 1, 2, 3, 4$ states.](image)

**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.

⇒ 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)
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, ms (where ms = -1/2 and +1/2)