4E : The Quantum Universe

Lecture 26, May 17
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Radial Probability Distribution $P(r) = r^2 R(r)$

Because $P(r) = r^2 R(r)$; No matter what $R(r)$ is for some $n$, The prob. Of finding electron inside the nucleus = 0!!

<table>
<thead>
<tr>
<th>$n = 1$</th>
<th>$l = 0$</th>
<th>$R_{10} = \frac{2}{\sqrt{2}a_0} e^{-r/a_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n = 2$</td>
<td>$l = 0$</td>
<td>$R_{20} = \frac{1}{\sqrt{2}a_0} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$</td>
</tr>
<tr>
<td></td>
<td>$l = 1$</td>
<td>$R_{21} = \frac{1}{2\sqrt{6}a_0} \frac{r}{a_0} e^{-r/3a_0}$</td>
</tr>
<tr>
<td>$n = 3$</td>
<td>$l = 0$</td>
<td>$R_{30} = \frac{2}{3\sqrt{3}a_0} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$</td>
</tr>
<tr>
<td></td>
<td>$l = 1$</td>
<td>$R_{31} = \frac{8}{27\sqrt{6}a_0} \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0}$</td>
</tr>
<tr>
<td></td>
<td>$l = 2$</td>
<td>$R_{32} = \frac{4}{8\sqrt{30}a_0} \frac{r^2}{a_0^2} e^{-r/3a_0}$</td>
</tr>
<tr>
<td>$l$</td>
<td>$m$</td>
<td>Spherical harmonics</td>
</tr>
<tr>
<td>----</td>
<td>----</td>
<td>---------------------</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>$Y_{00} = \sqrt{\frac{1}{4\pi}}$</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>$Y_{11} = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta$</td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
<td>$Y_{1-1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}$</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>$Y_{22} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\phi}$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>$Y_{21} = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>$Y_{2-1} = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{-i\phi}$</td>
</tr>
<tr>
<td>1</td>
<td>-2</td>
<td>$Y_{2-2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{-2i\phi}$</td>
</tr>
</tbody>
</table>
Excited States \((n>1)\) of Hydrogen Atom : Birth of Chemistry!

Features of Wavefunction in \(\theta \& \phi\):

Consider \(n = 2, \ l = 0 \Rightarrow \psi_{200} = \) Spherically Symmetric (last slide)

Excited States (3 \& each with same \(E_n\)):

\(\psi_{211}, \psi_{210}, \psi_{21-1}\) are all \(2p\) states

\[
\psi_{211} = R_{21} Y_{1}^{0} = \left( \frac{1}{\sqrt{\pi}} \right) \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Z}{8} \right) \left( \frac{r}{a_0} \right) e^{-2r/a_0} \sin \theta e^{i\phi}
\]

| \(|\psi_{211}\|^2 = |\psi_{211}\rangle \langle \psi_{211}| \propto \sin^2 \theta | \]

Max at \(\theta = \frac{\pi}{2}\), min at \(\theta = 0\); Symm in \(\phi\)

What about \((n=2, \ l=1, m_l = 0)\)

\(\psi_{210} = R_{21}(r) Y_{1}^{0} (\theta, \phi) ;\)

\(Y_{1}^{0} (\theta, \phi) \propto \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta ;\)

Function is max at \(\theta = 0\), min at \(\theta = \frac{\pi}{2}\)

We call this \(2p_z\) state because of its extent in \(z\)
Excited States \((n>1)\) of Hydrogen Atom: Birth of Chemistry!

Remember Principle of Linear Superposition

for the TISE which is basically a simple differential equation:

\[
-\frac{\hbar^2}{2m} \nabla^2 \psi + U \psi = E \psi
\]

Principle of Linear Superposition \(\Rightarrow\) If \(\psi_1\) and \(\psi_2\) are sol. of TISE then a "designer" wavefunction made of linear sum

\[\psi' = a \psi_1 + b \psi_2\]

is also a sol. of the diff. equation!

To check this, just substitute \(\psi'\) in place of \(\psi\)

& convince yourself that

\[
-\frac{\hbar^2}{2m} \nabla^2 \psi' + U \psi' = E \psi'
\]

The diversity in Chemistry and Biology DEPENDS on this superposition rule
**Designer Wave Functions: Solutions of S. Eq!**

Linear Superposition Principle means allows me to "cook up" wavefunctions

\[ \psi_{2p_x} = \frac{1}{\sqrt{2}} [\psi_{211} + \psi_{21-1}] \] ......has electron "cloud" oriented along x axis

\[ \psi_{2p_y} = \frac{1}{\sqrt{2}} [\psi_{211} - \psi_{21-1}] \] ......has electron "cloud" oriented along y axis

So from 4 solutions \( \psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1} \rightarrow 2s, 2p_x, 2p_y, 2p_z \)

Similarly for n=3 states ...and so on ...can get very complicated structure in \( \theta & \phi \)......which I can then mix & match to make electrons "most likely" to be where I want them to be!
Designer Wave Functions: Solutions of S. Eq!

\[ n = 2, \ell = 1, m_\ell = \pm 1 \quad n = 3, \ell = 1, m_\ell = 0 \quad n = 3, \ell = 2, m_\ell = 0 \]
Cross Sectional View of Hydrogen Atom prob. densities in r, θ, φ
Birth of Chemistry (Can make Fancy Bonds → Overlapping electron “clouds”)

What’s the electron “cloud”: It’s the Probability Density in r, θ, φ space!
More Radial Probabilities $P(r)$ Vs. $r/a_0$

$P(r) \propto r^2|\psi|^2$

Net Prob. densities for $n=2$ states

- spherically symmetric
- dumbbell
- Doughnut (toroid)
Radiative Transitions: An Impromptu Discussion

• Concepts
  – Write and use the wavefunctions which arise as solutions of the time-dependent Schrodinger equation
  – Use concept of linear superposition of time-dependent wavefunctions
  – Calculate expectation value for $<x>$, when is it time-dependent?

• See slides (posted) from Lecture 27 (See also Modern Physics by Beiser, chapter 6, sections 8-9, page 214. Text available from the E-reserve page as pdf files)