Lecture 12

Radial Dependence of Hydrogen Wave Function

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Review: Angular Momentum

Angular momentum operators:

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right)$$

Angular eigenstates:

$$\hat{L}_z Y_{lm}(\theta, \phi) = m\hbar \, Y_{lm}(\theta, \phi)$$

$$\hat{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\,\hbar^2 \, Y_{lm}(\theta, \phi)$$

$Y_{lm}(\theta, \phi)$ represents a state with

$$|\vec{L}| = \sqrt{l(l+1)}\hbar$$

$$L_z = m\hbar$$

Review: Properties of QM Angular Momentum

- A particle can be prepared in a state with definite magnitude of angular momentum and definite value of angular momentum in some direction (conventionally chosen to be the z-axis).

- If a particle has a definite angular momentum along some direction, it can not have a definite angular momentum along any other direction.

- As a result, the angular momentum cannot point in a definite direction. If it did, it would have a definite value along that direction, say z, and a definite definite value along x and y also, namely, zero.

- When the angular momentum is measured along any direction, the only possible values that will be measured are the various possible values of $m\hbar$. If the particle is in a state of definite angular momentum along a particular direction then that value of $m\hbar$ is certain to be measured in that direction.

- If the particle is not in a state of definite angular momentum along that direction then the various values of $m\hbar$ will be measured with relative probabilities dependent on the state.

Example of $l = 1$

For $l = 1$, $m = 1$:

$$|\vec{L}| = \sqrt{2}\,\hbar \qquad \text{and} \qquad L_Z = \hbar$$

If we measure L along any axis, the only possible values that we can get are $-\hbar,\ 0,\ +\hbar$.

$$\Rightarrow \qquad P_z(+\hbar) = 1 \qquad P_z(0) = 0 \qquad P_z(-\hbar) = 0$$

What about for a measurement along the x-axis?

Example of $l = 1$ (cont.)

For $l = 1$, $m = 1$:

$$|\vec{L}| = \sqrt{2}\,\hbar \qquad \text{and} \qquad L_Z = \hbar$$

$$\Rightarrow \qquad |\vec{L}|^2 = L_x^2 + L_y^2 + L_z^2 = 2\hbar^2$$

$$L_x^2 + L_y^2 = 2\hbar^2 - L_z^2 = \hbar^2 \qquad \Rightarrow \qquad \langle L_x^2 \rangle + \langle L_y^2 \rangle = \hbar^2$$

$$\langle L_x^2 \rangle = \langle L_y^2 \rangle \Rightarrow \qquad \langle L_x^2 \rangle = \frac{\hbar^2}{2}$$

$$\langle L_x^2 \rangle = \hbar^2 P_x(+\hbar) + \hbar^2 P_x(-\hbar)$$

$$P_x(+\hbar) = P_x(-\hbar) \qquad \Rightarrow \qquad P_x(+\hbar) = P_x(-\hbar) = \frac{1}{4}$$

$$P_x(+\hbar) + P_x(0) + P_x(-\hbar) = 1 \qquad \Rightarrow \qquad P_x(0) = \frac{1}{2}$$

$$\Rightarrow \qquad P_x(+\hbar) = \frac{1}{4} \qquad P_x(0) = \frac{1}{2} \qquad P_x(-\hbar) = \frac{1}{4}$$

The Radial Part of the Hydrogen Atom Wave Function

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r} - \frac{2m}{\hbar^2}\left[V(r) - E\right] + \frac{\lambda}{r^2}\right) R(r) = 0$$

$$\left(-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\lambda}{r^2}\right] + V(r) - E\right) R(r) = 0$$

$$\left(-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1)}{r^2}\right] + V(r) - E\right) R(r) = 0$$

$$\left(-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1)}{r^2}\right] - \frac{e^2}{4\pi\epsilon_0 r} - E\right) R(r) = 0$$

$$\left(-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right] + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} - E\right) R(r) = 0$$

Transverse Momentum

$$-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right]R(r)=\frac{p_r^2}{2m}R(r)$$

$$\frac{l(l+1)\hbar^2}{2mr^2}R(r)=\frac{L^2}{2mr^2}R(r)=\frac{p_\perp^2 r^2}{2mr^2}R(r)=\frac{p_\perp^2}{2m}R(r)$$

$$\left(-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}-\frac{l(l+1)}{r^2}\right]+V(r)-E\right)R(r)$$

$$=\left(\frac{p_r^2+p_\perp^2}{2m}+V(r)-E\right)R(r)=\left(\frac{p^2}{2m}+V(r)-E\right)R(r)=0$$

Centrifugal Barrier

$$\left(-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right]+\frac{l(l+1)\hbar^2}{2mr^2}-\frac{e^2}{4\pi\epsilon_0 r}-E\right)R(r)=0$$

$$\frac{l(l+1)\hbar^2}{2mr^2}$$ is like a positive potential energy term

It is referred to as the centrifugal barrier.

It acts like a repulsive force that is larger for higher angular momentum states.

It has the effect of causing higher angular momentum states to be further from the nucleus.

Quantized Energies

When the radial equation is solved it's found that solutions exist only for certain quantized values of the energy

$$E = -\frac{1}{2} mc^2 \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 \frac{1}{(n_r + l + 1)^2} \qquad \text{with} \qquad n_r = 0,\ 1,\ 2,\ \cdots$$

Define $n = n_r + l + 1$:

$$E = -\frac{1}{2} mc^2 \left(\frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 \frac{1}{n^2}$$

with $\qquad n = 1,\ 2,\ 3,\ \cdots \qquad$ and $\qquad l \leq n - 1$

Solution for Large Values of r

$$\left(-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right]+\frac{l(l+1)\hbar^2}{2mr^2}-\frac{e^2}{4\pi\epsilon_0 r}-E\right)R(r)=0$$

For large values of r: $$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2}-E\right)R(r)=0$$

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}R(r)=\frac{2m|E|}{\hbar^2}R(r)$$

$$R(r)=C_1e^{Ar}+C_2e^{-Ar}$$ with $A=\sqrt{\frac{2m|E|}{\hbar^2}}=\frac{mc\alpha}{n\hbar}=\frac{1}{na_0}$

to keep $R(r)$ finite for all r we must have $C_1=0$

$$\Rightarrow \quad R(r)=Ce^{-r/na_0} \quad \text{for large } r$$

Solution for Small Values of r

$$\left(-\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right]+\frac{l(l+1)\hbar^2}{2mr^2}-\frac{e^2}{4\pi\epsilon_0 r}-E\right)R(r)=0$$

For small values of r: $$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}-\frac{l(l+1)}{r^2}\right)R(r)=0$$

try $R(r)=Cr^b$

$$b(b-1)r^{b-2}+2br^{b-2}-l(l+1)r^{b-2}=0 \quad\Rightarrow\quad b(b+1)-l(l+1)=0$$

$\Rightarrow$ possible values for b are: $b=l$ and $b=-l-1$

$$R(r)=C_1 r^l + C_2 r^{-l-1}$$

to keep $R(r)$ finite for $r=0$ we must have $C_2=0$

$\Rightarrow$ $R(r)=Cr^l$ for small r

The Radial Wave Functions

$R(r)$ depends on the quantum numbers n and l

In general:

$$R_{nl}(r) \propto \left(\frac{r}{a_0}\right)^l \left(\text{polynomial in } \frac{r}{a_0} \text{ of order } n-l-1\right) e^{-r/na_0}$$

The first few R's:

$$R_{10}(r) = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$R_{20}(r) = 2\left(\frac{1}{2a_0}\right)^{3/2} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{1}{2a_0}\right)^{3/2} \left(\frac{r}{a_0}\right) e^{-r/2a_0}$$

Summary

$$u(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

$$E = -\frac{1}{2}mc^2\left(\frac{e^2}{4\pi\epsilon_0\hbar c}\right)^2\frac{1}{n^2} \qquad n = 1,\ 2,\ 3,\ \cdots$$

$$|\vec{L}| = \sqrt{l(l+1)}\hbar \qquad l = 0,\ 1,\ 2,\ \cdots,\ n-1$$

$$L_z = m\hbar \qquad m = -l,\ \cdots, 1,\ 0,\ 1,\ \cdots,\ l$$

Energy Levels and Degenracy

Energy depends only upon n.

$$E = -\frac{1}{2}mc^2\left(\frac{e^2}{4\pi\epsilon_0\hbar c}\right)^2\frac{1}{n^2} \qquad n = 1,\ 2,\ 3,\ \cdots$$

For each value of n there are n possible value of l.

$$l = 0,\ 1,\ 2,\ \cdots,\ n-1$$

For each value of l there are $2l+1$ possible value of m.

$$m = -l,\ \cdots,1,\ 0,\ 1,\ \cdots,\ l$$

$\Rightarrow$ degeneracy of the nth level is $\displaystyle\sum_{l=0}^{n-1}(2l+1) = n^2$

Probabilities

In spherical coordinates, the differential volume element is:

$$(r\sin\theta \mathrm{d}\phi)(r\mathrm{d}\theta)(\mathrm{d}\phi) = r^2 \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\phi \,\mathrm{d}r$$

$$P(\theta,\phi) = |Y_{lm}(\theta,\phi)|^2 \sin\theta$$

$$P(r) = r^2 |R_{nl}(r)|^2$$

Normalization:

$$\int_0^{\pi}\int_0^{2\pi} |Y_{lm}(\theta,\phi)|^2 \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\phi = 1$$

$$\int_0^{\infty} r^2 |R_{nl}(r)|^2 \,\mathrm{d}r = 1$$