

Ok we have finally finished! The 1  
3D energy eigenstates of the hydrogen  
atom are,

$$|n\ell m\rangle \doteq R_{n\ell}(r) Y_{\ell}^m(\theta, \phi)$$

Moreover these energy eigenstates are simultaneous  
eigenstates of  $L^2$  &  $L_z$ !

$$H|n\ell m\rangle = -\frac{13.6\text{eV}}{n^2}|n\ell m\rangle$$

$$L^2|n\ell m\rangle = \ell(\ell+1)\hbar^2|n\ell m\rangle$$

$$L_z|n\ell m\rangle = m\hbar|n\ell m\rangle$$

The position representations of these eigenstates  
require knowing  $n, \ell, m$ . These states  
are tabulated in many QM books.

$$|100\rangle \doteq \psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{z}{a_0}\right)^{3/2} e^{-zr/a_0}$$

$$|200\rangle \doteq \psi_{200} = \frac{1}{\sqrt{\pi}} \left(\frac{z}{2a_0}\right)^{3/2} \left[1 - \frac{zr}{2a_0}\right] e^{-zr/2a_0}$$

$$|210\rangle \doteq \psi_{210} = \frac{1}{2\sqrt{\pi}} \left(\frac{z}{2a_0}\right)^{3/2} \frac{zr}{a_0} e^{-zr/2a_0} \cos\theta$$

$$|21\pm 1\rangle \doteq \psi_{21\pm 1} = \mp \frac{1}{2\sqrt{2}\pi} \left(\frac{z}{2a_0}\right)^{3/2} \frac{zr}{a_0} e^{-zr/2a_0} \sin\theta e^{\pm i\phi}$$

etc....

## Properties of $\psi_{nlm}$ Solutions (2)

as these results are compiled in tables it's important for us to know how to use them rather than derive them.

### ① Normalization

$$1 = \langle nlm | nlm \rangle = \int |\psi_{nlm}(\theta, \phi)|^2 dV$$

which is a full 3D integral,

$$\langle nlm | nlm \rangle = \int_0^\infty \int_0^{2\pi} \int_0^\pi |\psi_{nlm}(\theta, \phi)|^2 r^2 \sin\theta d\theta d\phi dr$$

Note that  $R_{nl}$  &  $Y_{lm}$  have been normalized separately.

$$\langle nlm | nlm \rangle = \underbrace{\left\{ \int_0^\infty r^2 |R_{nl}|^2 dr \right\}}_{=1} \underbrace{\left\{ \int_0^{2\pi} \int_0^\pi |Y_{lm}|^2 \sin\theta d\theta d\phi \right\}}_{=1}$$

Turns out that makes some calculations much easier. (3)

(2) The probability density is simply the absolute square of  $\psi_{nlm}$ ,

$$P(r, \theta, \phi) = |\psi_{nlm}(r, \theta, \phi)|^2 = |R_{nl}(r) Y_l^m(\theta, \phi)|^2$$

By multiplying by a volume element we find the probability the particle is in some volume,

$$\begin{aligned} P(r, \theta, \phi) dV &= |\psi_{nlm}(r, \theta, \phi)|^2 dV \\ &= |R_{nl}(r) Y_l^m(\theta, \phi)|^2 r^2 \sin \theta d\theta d\phi dr \end{aligned}$$

Example: Probability of finding the electron in a sphere of radius  $a_0$  given it is in the ground state,

$$|100\rangle \equiv \psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad \left( \begin{array}{l} \text{no } z \text{ b/c} \\ \text{Hydrogen } z=1 \end{array} \right)$$

(4)

$$\begin{aligned} \text{Prob}_{r < a_0} &= \int_{\substack{\text{all } \theta, \phi \\ r < a_0}} P(r, \theta, \phi) dV \\ &= \int_0^{a_0} \int_0^{2\pi} \int_0^\pi P(r, \theta, \phi) r^2 \sin\theta d\theta d\phi dr \\ &= \int_0^a \int_0^{2\pi} \int_0^\pi |R_{n\ell}(r) Y_\ell^m(\theta, \phi)|^2 r^2 \sin\theta d\theta d\phi dr \\ &= \left\{ \int_0^a |R_{n\ell}(r)|^2 r^2 dr \right\} \underbrace{\left\{ \int_0^{2\pi} \int_0^\pi |Y_\ell^m(\theta, \phi)|^2 \sin\theta d\theta d\phi \right\}}_{= 1 \text{ just } Y_\ell^m \text{ normalized!}} \end{aligned}$$

$$\text{Prob}_{r < a_0} = \int_0^a |R_{n\ell}(r)|^2 r^2 dr$$

for the ground state  $n=1, \ell=0,$

$$= \int_0^a |R_{10}(r)|^2 r^2 dr = \int_0^a r^2 \left(\frac{4}{a_0^3}\right) e^{-2r/a_0} dr$$

Wolfram

$$\text{Prob}_{r < a_0} = 1 - 5e^{-2} \approx 0.323$$