Hydrogen-like Solutions go Brrrrrr...

$|nlm\rangle \doteq R_{nl}(r)\, Y_l^m(\theta,\phi)$

H, L^2, L_z

$$\boxed{\begin{aligned} H|nlm\rangle &= \frac{-13.6\,eV}{n^2}|nlm\rangle \quad \text{for Hydrogen} \\ L^2|nlm\rangle &= l(l+1)\hbar^2|nlm\rangle \\ L_z|nlm\rangle &= m\hbar|nlm\rangle \end{aligned}}$$

Position Representations

$\langle \vec{r}|nlm\rangle \rightarrow$ QM Books

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

Bohr Radius

Hydrogen $Z=1$

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

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

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

$$|21\pm1\rangle \doteq \psi_{21\pm1} = \mp\frac{1}{2\sqrt{2\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\underline{\sin\theta}\,\underline{e^{\pm i\phi}}$$

etc.... QM Books or online

Properties of Solutions

① Normalization

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

$$= \int_0^\infty\int_0^{2\pi}\int_0^\pi|\psi_{nlm}(r,\theta,\phi)|^2\underbrace{r^2\sin\theta\, d\theta\, d\phi\, dr}_{dV \text{ spherical coords.}}$$

Normalized R_{nl} & Y_l^m separately

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

② Probability density → absolute square ψ_{nlm}

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

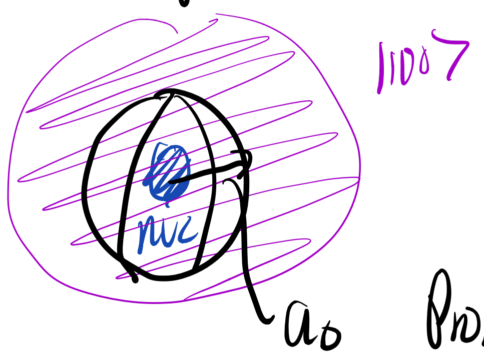
$$= |R_{nl}(r)\, Y_l^m(\theta,\phi)|^2$$

Probability of occupying dV

$$P(r,\theta,\phi)\,dV = |R_{nl}(r)\, Y_l(\theta,\phi)|^2 \underbrace{r^2 \sin\theta\, d\theta\, d\phi\, dr}_{dV \text{ spherical}}$$

Example: $|100\rangle$

what's prob. that we find particle in a sphere of radius, a_0.



$Z = 1$

Prob?

$$|100\rangle \doteq \psi_{100} = \underline{\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}}$$

$$\text{Prob}_{r<a_0} = \int \rho(r,\theta,\phi)\, dV$$

$\theta: 0 \to \pi$

$\phi: 0 \to 2\pi$

$r: 0 \to a_0$

$$= \int_0^{a_0} \int_0^{2\pi} \int_0^{\pi} \rho(r,\theta,\phi)_{100}\, r^2 \sin\theta\, d\theta\, d\phi\, dr$$

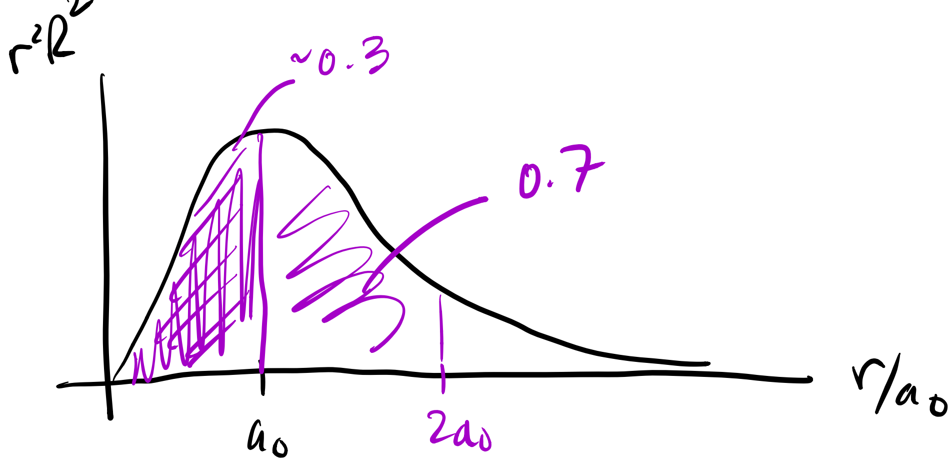
$$\Rightarrow = \int_0^{a_0}\int_0^{2\pi}\int_0^{\pi} \left| R_{10}(r)\, Y_0^0(\theta,\phi)\right|^2 r^2 \sin\theta \, d\theta\, d\phi\, dr$$

$$= \int_0^{a_0} r^2 |R_{10}(r)|^2 dr \underbrace{\int_0^{2\pi}\int_0^{\pi} |Y_0^0(\theta,\phi)|^2 \sin\theta \, d\theta\, d\phi}_{=1}$$

$$\text{Prob}_{r<a_0} = \int_0^{a_0} r^2 \left(\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}\right)^2 dr$$

$$= \frac{1}{\pi a_0^3}\int_0^{a_0} r^2 e^{-2r/a_0} dr$$

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



$|n\ell m\rangle \Leftarrow$ energy eigenstates

↳ time evolution prescription works.

Time Evolve

$$|\psi(t)\rangle \doteq \psi_{n\ell m}(r,\theta,\phi,t)$$

$$= R_{n\ell}(r)\, Y_\ell^m(\theta,\phi)\, \underbrace{e^{-iE_n t/\hbar}}_{\text{prescription}}$$

$$E_n = -\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{m_e}{\hbar^2}$$

$$Z=1 \quad E_n = -\frac{C}{n^2} \qquad C = 13.6\,\text{eV}$$

Superposition States

$$|\psi(t)\rangle \doteq \psi(r,\theta,\phi,t)$$

$$= \sum_{n,\ell,m} c_{n\ell m} R_{n\ell}(r)\, Y_\ell^m(\theta,\phi)\, e^{-iE_n t/\hbar}$$

for given $n \to$ diff. ℓ's $\to$ diff m's | degeneracy $\sim n^2$

$|100\rangle \to E_1$

$|200\rangle$ $|211\rangle$
$|210\rangle$ $|21{-}1\rangle$ $\to E_2$ $n^2 \sim 2^2 = 4$

$$\boxed{\begin{aligned} C_{n\ell m} &= \langle n\ell m | \Psi(t=0)\rangle \\ &= \int_0^\infty r^2 dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \, R_{n\ell}^* Y_\ell^{m*} \Psi \end{aligned}}$$

Example: $1s$ & $2p_0$ Time Evolution

$1s \leftarrow |100\rangle$, $2p_0 \leftarrow |210\rangle$

$$|\Psi(0)\rangle = \frac{1}{\sqrt{2}}|100\rangle + \frac{1}{\sqrt{2}}|210\rangle$$

$$|\psi(0)\rangle \doteq \underbrace{\frac{1}{\sqrt{2}}\psi_{100}}_{\text{normalized!}} + \underbrace{\frac{1}{\sqrt{2}}\psi_{210}}$$

$$= \frac{1}{\sqrt{2}}\left(\underline{\frac{1}{\sqrt{\pi a_0^3}}e}^{-r/a_0}\right) + \frac{1}{\sqrt{2}}\left(\frac{1}{2\sqrt{\pi}}\left(\frac{1}{2a_0}\right)^{3/2}\frac{r}{a_0} e^{-r/2a_0}\cos\theta\right)$$

$$|\psi(0)\rangle = \frac{1}{\sqrt{2\pi a_0^3}}e^{-r/a_0} + \frac{1}{\pi a_0^3}\frac{r\cos\theta}{8a_0}e^{-r/2a_0}$$

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\psi_{100}e^{-iE_1t/\hbar} + \frac{1}{\sqrt{2}}\psi_{210}e^{-iE_2t/\hbar}$$

$$E_1 = -\frac{c}{n^2} \qquad c = 13.6\,eV$$

$$|\psi(t)\rangle = \frac{1}{\sqrt{2\pi a_0^3}}e^{-r/a_0}\underline{e^{-iE_1t/\hbar}}$$

$$+ \frac{1}{\sqrt{\pi a_0^3}}\frac{r\cos\theta}{8a_0}e^{-r/2a_0}\underbrace{e^{-iE_2t/\hbar}}_{e^{-i(E_2-E_1)t/\hbar}}$$

$$|\psi(t)\rangle = \frac{1}{\sqrt{2\pi a_0^3}} e^{-iE_1 t/\hbar} \times$$
$$\left(e^{-r/a_0} + \frac{r\cos\theta}{4\sqrt{2}a_0} e^{-r/2a_0} e^{-i(E_2-E_1)t/\hbar}\right)$$

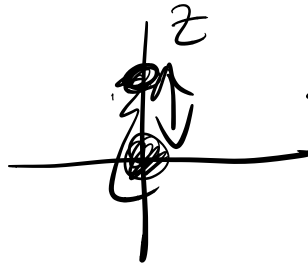
Prob dens. $= \langle\psi(t)|\psi(t)\rangle$

$$= \frac{1}{2\pi a_0^3}\left(e^{-2r/a_0} + \frac{r^2\cos^2\theta}{32 a_0^2} e^{-r/a_0}\right.$$
$$\left. + e^{-r/a_0}\frac{r\cos\theta}{4\sqrt{2} a_0} e^{-r/2a_0}\left(e^{-i\omega_{21}t} + e^{+i\omega_{21}t}\right)\right)$$

$\omega_{21} = E_2 - E_1/\hbar$ freq. transition.

$$e^{-i\omega_{21}t} + e^{+i\omega_{21}t} \propto \cos(\omega_{21}t)$$

osc.



~ electric dipole