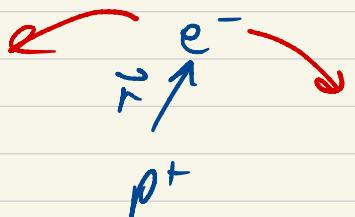


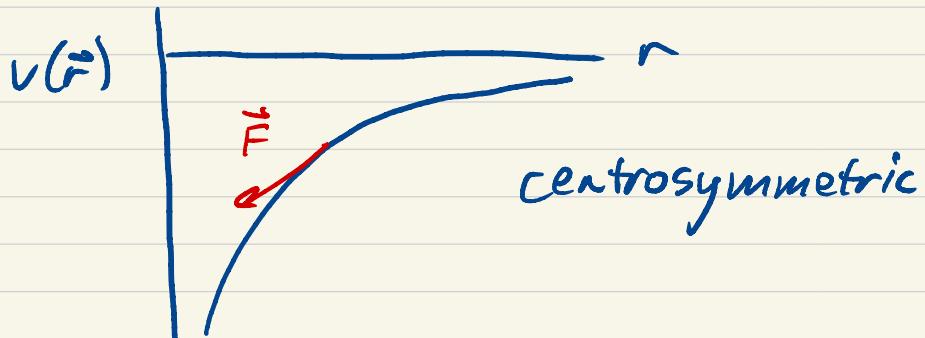
Hydrogen atom



opposite charge
Coulomb attraction

$$\vec{F} = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{|\vec{r}|^2}$$

$$V(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{|\vec{r}|}$$



Classically collapses. Wave property prevents that.

Schrödinger eq

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}|} \right\} \psi(\vec{r}) = E \psi(\vec{r})$$

mass? formally $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_p}$
 $m \approx m_e$

coordinate system? spherical
boundary conditions?

Θ, ϕ continuity

$\lim_{r \rightarrow \infty} \Psi(\vec{r}) = 0$ bound
square-integrable

Schrödinger eq ...

$$\left\{ -\frac{\hbar^2}{2mr^2} \hat{l}^2 - \frac{\hbar^2}{2mr^2} \left(\frac{\partial r^2}{\partial r} \frac{\partial}{\partial r} \right) - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r} \right\} \Psi(r, \theta, \phi)$$

rigid rotor! radial KE $V(r) = E \Psi(r, \theta, \phi)$

Separate variables!

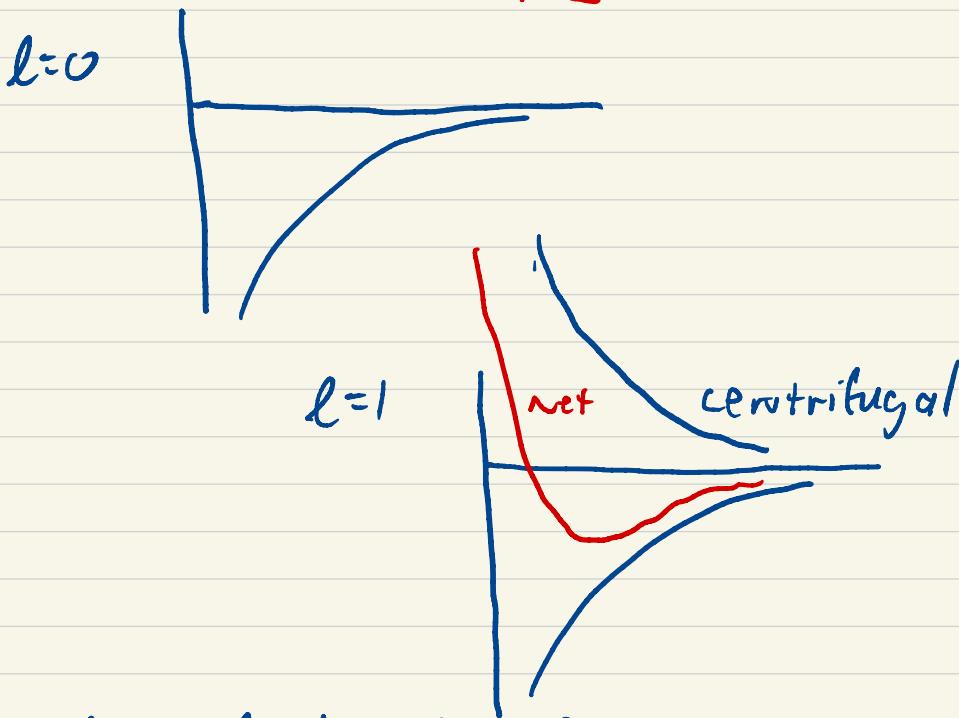
appearance of \hat{l}^2 suggests spherical harmonics, which works!

$$\Psi(r, \theta, \phi) = R(r) Y_{lm}(\theta, \phi)$$

substitute

$$\left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \left[\frac{d}{dr} r^2 \frac{d}{dr} \right] + \frac{\hbar^2 l(l+1)}{2m r^2} - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r} \right] R_e(r)$$

radial KE angular pot'l = $E R_e(r)$
KE



As $l \uparrow$, harder to get near nucleus

$$R_{nl}(r) = N_{nl} e^{-x/2} x^l L_{nl}(x)$$

norm exp cent polynomials
associated associated Laguerre polynomials

$$x = \frac{2r}{n\alpha_0} \quad a_0 = \frac{\hbar^2}{m_e} \left(\frac{4\pi e}{e^2} \right) = 0.529 \text{ \AA}^0$$

Bohr radius

$$\Psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r) Y_{lm_l}(\theta, \phi)$$

$$E_n = -\frac{E_H}{2} \frac{1}{n^2} \quad E_H = \frac{\hbar^2}{m_e a_0^2} = 27.212 \text{ eV}$$

$n = 1, 2, 3, \dots$ principal
 size, # of radial nodes
 total energy

K, L, M ... "shell"

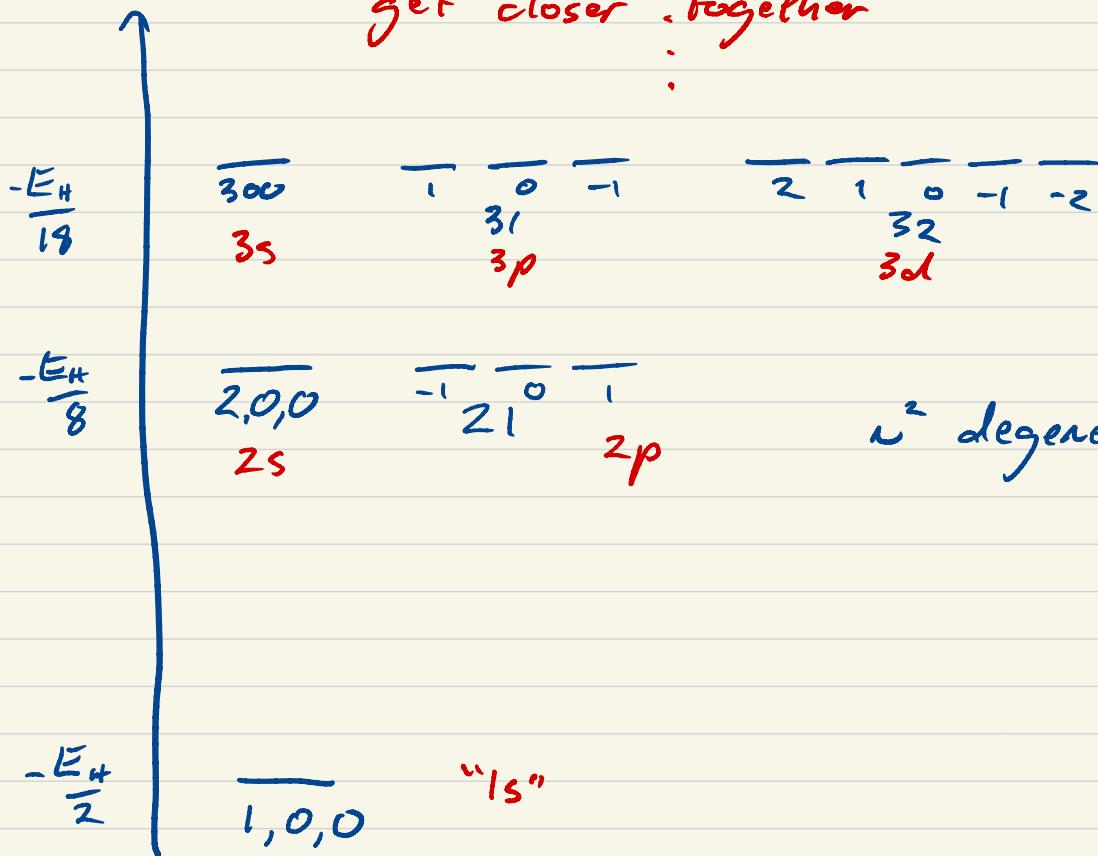
$l = 0, 1, \dots, n-1$ angular
 shape, # of angular nodes
 angular momentum
 s, p, d "subshell"

$m_l = -l, -l+1, \dots, 0, \dots l$ azimuthal
 orientation
 z-component of $\vec{l}\vec{l}$

Same as original Bohr result!

But much more detailed info about atomic structure.

get closer together



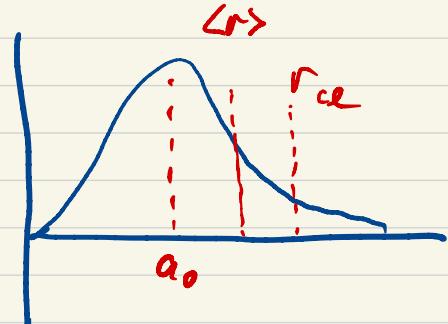
Relativistic treatment reveals spin of electron

$$s = \frac{1}{2} \quad m_s = \pm \frac{1}{2}$$

100 "1s"

$$Y_{00}(\theta, \phi) = \text{const} \quad \text{spherical}$$

$$R_{10}(r) = e^{-r}$$



Probability to be distance r from nucleus:

$$\begin{aligned} P(r) &= \int_0^{2\pi} \int_0^{\pi} Y_{00}(\theta, \phi)^2 R(r) r^2 \sin \theta dr d\theta d\phi \\ &= r^2 R^2(r) \quad \text{in general true} \end{aligned}$$

$$\frac{dP(r)}{dr} = 0 \Rightarrow r_{mp} = a_0 !$$

same as Bohr orbit

$$\langle r \rangle = \int_0^{\infty} r P(r) dr$$

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

$$= \underbrace{(3n^2 - l(l+1))}_{\text{red line}} \cdot \frac{a_0}{2} \cdot Z$$

$$r_{ce} : V(r) = -\frac{E_n}{Z}$$

$$-\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r_{ce}} = -\frac{1}{2} \frac{\hbar^2}{m_e a_0^2}$$

$$= -\frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{a_0}$$

$$\boxed{r_{ce} = 2a_0}$$

Kinetic & Potential energy

$\langle \hat{T} \rangle$, $\langle \hat{V} \rangle$ in principle could
grind out. Simplified by considering
virtual theorem

If potential is of the form $V = \alpha r^\beta$,
then $\langle T \rangle = \frac{\beta}{2} \langle V \rangle$

For H atom, $\beta = -1$

$$\rightarrow \langle T \rangle = -\frac{1}{2} \langle V \rangle$$

But $\langle T \rangle + \langle V \rangle = \langle E \rangle$

$$\langle T \rangle - 2 \langle T \rangle = \langle E \rangle$$

$$\langle T \rangle = -\langle E \rangle = \frac{E_H}{2} \cdot \frac{1}{n^2} > 0$$

$$\langle V \rangle = -E_H \cdot \frac{1}{n^2} \quad \text{ZPE}$$

Is moving fastest.

example

$$E_{1s} = -13.6 \text{ eV}$$

$$\langle T \rangle_{1s} = 6.8 \text{ eV}$$

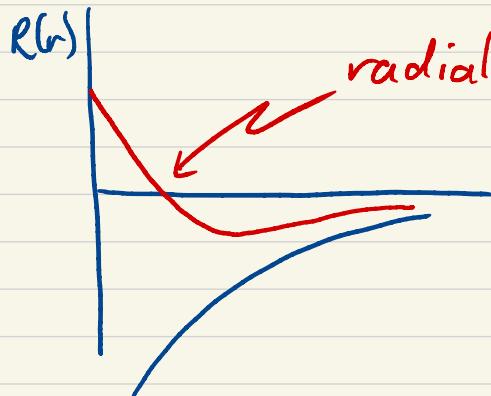
$$\langle v^2 \rangle^{\frac{1}{2}} = 4 \times 10^6 \text{ m/s} = 0.01 c$$

K.E scales linearly w/Z. For
heavier elements Is moves relativistically.

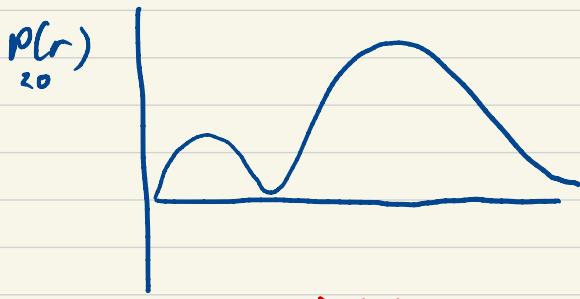
200 "2s"

$$Y_{00}(\theta, \phi) = \text{constant}$$

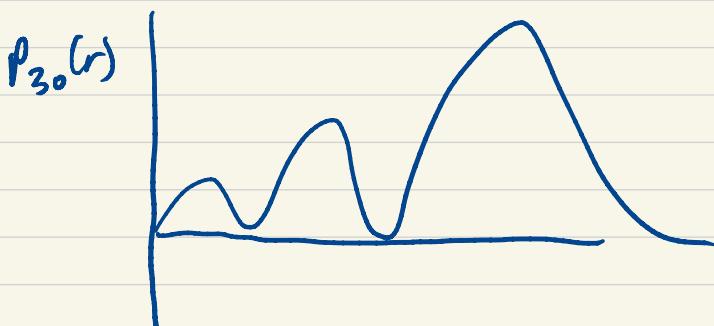
$$R_{20}(r) \propto (1 - \frac{r}{2}) e^{-r/2a_0}$$



In general,
radial node =
 $n - l - 1$



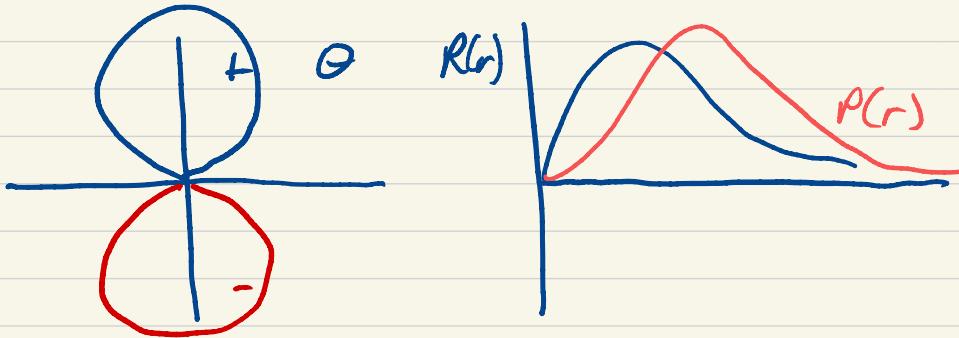
$\langle r \rangle = 6a_0$
way bigger
than 2s



ZIO "2p"

$$\psi_{210} \propto \cos\theta \ r e^{-r/2}$$

↑ lobe shape ↑ vanishes
 @ origin



$$\langle r \rangle_{2p} = 5a_0 < \langle r \rangle_{2s}$$

More compact on average.

...

d orbitals.

Selection rules

$$\langle 4_{\text{initial}} | \hat{r} | 4_{\text{final}} \rangle = 0 \quad \underline{\text{unless}}$$

$$\Delta l = \pm 1 \quad \Delta m_l = 0, \pm 1$$

$$\Delta m_s = 0$$

(emerges from electron conservation of angular momentum)

Example

$$\frac{P(n=2)}{P(n=1)} = \frac{4 e^{+(E_H/2) \cdot \frac{1}{4}/kT}}{1 e^{+(E_H/2)/kT}}$$

$$= 4 e^{-(E_H/2) \cdot \frac{3}{4}/kT}$$

$$\approx 4 e^{-9/0.025} = 0 !!$$

@ 298 K

Allowed transitions?

$$100 \rightarrow 210$$

$$\rightarrow 310$$

$$\rightarrow 410$$

Fluorescence, Phosphorescence & forbidden transitions