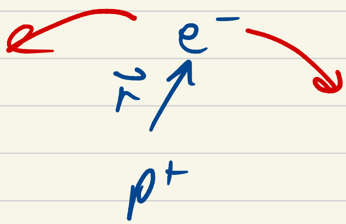
Hydrogen atom



opposite charge
Coulomb attraction

$$\vec F = \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{|\vec r|^2} \qquad V(\vec r) = -\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{|\vec r|}$$

centrosymmetric

Classically collapses. Wave property prevents that.

Schrödinger eq

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec r|}\right\}\psi(\vec r) = E\psi(\vec r)$$

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

$$\mu \approx m_e$$

coordincte system? spherical

boundary conditions?

θ, ϕ continuity

$\lim_{r\to\infty} \psi(\vec{r}) = 0$ bound

square-integrable

Schrödinger eq ...

$$\left\{ -\frac{\hbar^2}{2m} \cdot \frac{1}{r^2} \left[\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \hat{l}^2 \right] - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r} \right\} \psi(r,\theta,\phi)$$
$$= E\,\psi(r,\theta,\phi)$$

Separate variables!

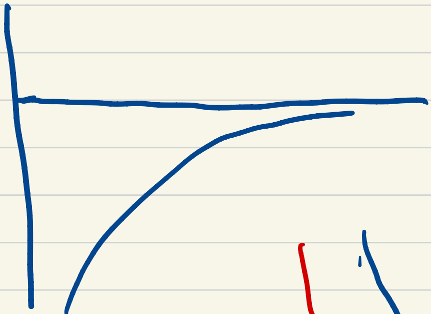
$$\psi(r,\theta,\phi) = R(r)\, Y_{lm}(\theta,\phi)$$

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

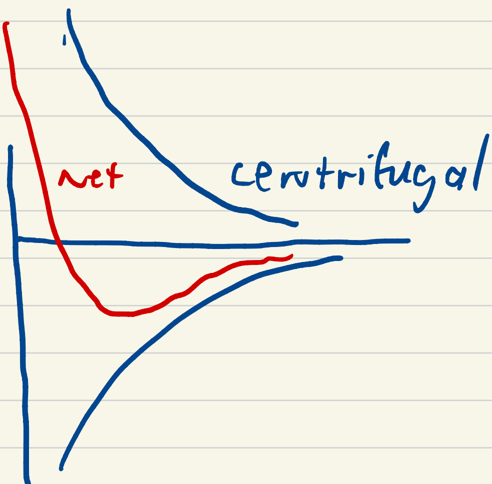
substitute

$$\left[\underbrace{-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right]}_{\text{radial KE}}+\underbrace{\frac{\hbar^2 l(l+1)}{2m_e r^2}}_{\text{angular KE}}\underbrace{-\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r}}_{\text{pot'l}}\right]R_l(r) = E\,R_l(r)$$

$l=0$



$l=1$



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

$$\Rightarrow R_{nl}(r) = \underbrace{N_{nl}}_{\text{norm}}\,\underbrace{e^{-x/2}}_{\text{exp}}\,\underbrace{x^l}_{\text{cent}}\,\underbrace{L_{nl}(x)}_{\text{polynomial}}$$

associated Laguerre polynomials

$x = \frac{2r}{n a_0}$ $\qquad a_0 = \frac{\hbar^2}{m_e}\left(\frac{4\pi\epsilon_0}{e^2}\right) = 0.529\,\mathring{A}$

Bohr radius

$$\psi_{n l m_l}(r,\theta,\phi) = R_{nl}(r)\, Y_{l m_l}(\theta,\phi)$$

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

$n = 1, 2, 3, \cdots$ principal

size, # of radial nodes

total energy

K, L, M... "shell"

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

shape, # of angular nodes

angular momentum

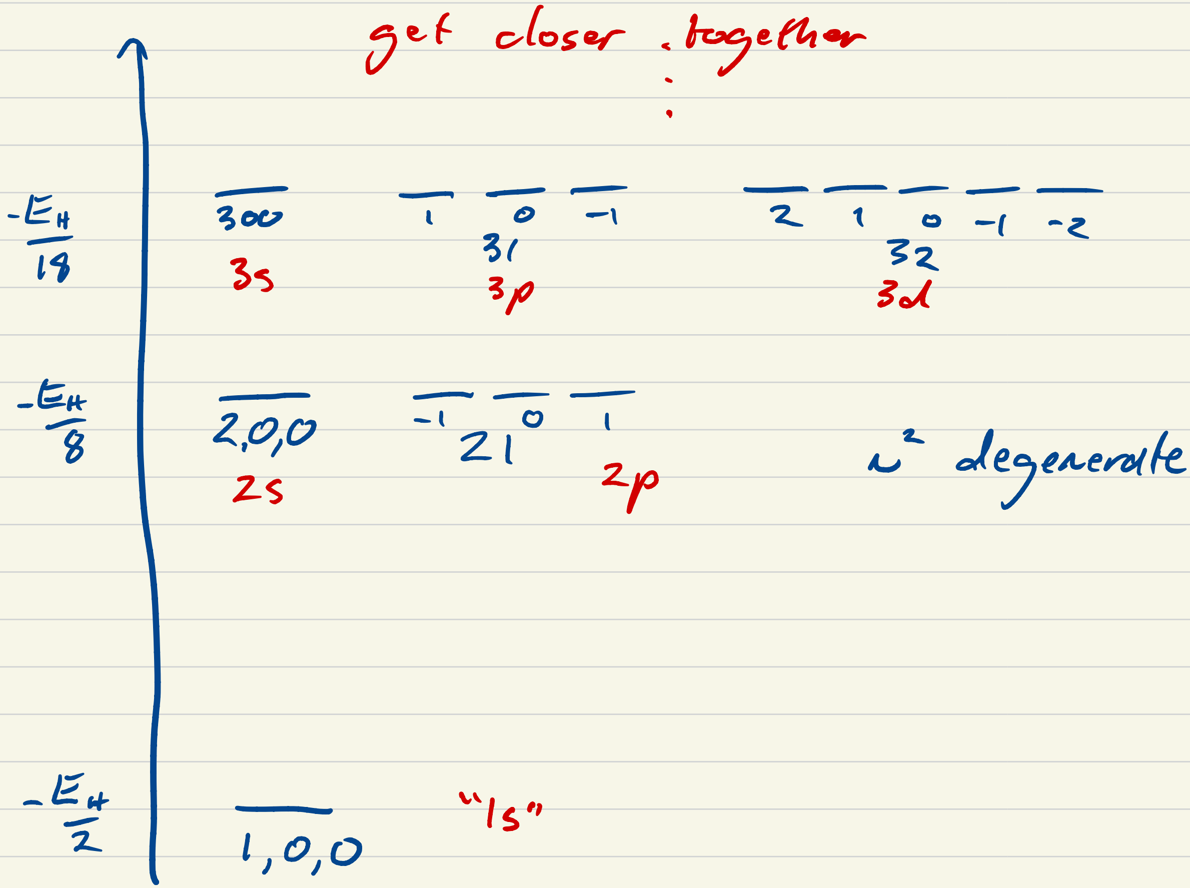
s, p, d "subshell"

$m_l = -l, -l+1, \cdots, 0, \cdots l$ azimuthal

orientation

z-component of $|\vec{l}|$

Same as original Bohr result!
But much more detailed info about atomic structure.

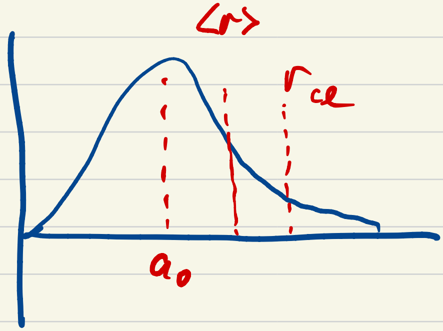


Relativistic treatment reveals spin of electron $s=\frac{1}{2}$ $m_s=\pm\frac{1}{2}$

100 "1s"

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

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



Probability to be distance r from nucleus:

$$P(r) = \int_0^{2\pi}\int_0^{\pi} Y_{00}(\theta,\phi)^2 R^2(r)\, r^2 \sin\theta \, dr\, d\theta\, d\phi$$

$$= r^2 R^2(r)$$ in general true

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

same as Bohr orbit

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

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

$$= \underline{\left(3n^2 - \ell(\ell+1)\right) \cdot \frac{a_0}{2} \cdot Z}$$

r_{ce} :

$$V(r) = -\frac{E_H}{Z}$$

$$-\frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{r_{ce}} = -\frac{1}{2} \frac{\hbar^2}{m_e a_0^2}$$

$$= -\frac{1}{2} \cdot \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{a_0}$$

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

Kinetic & Potential energy

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

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

For H atom, $\beta = -1$

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

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

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

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

ZPE

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

1s moving fastest.

<u>example</u>

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

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

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

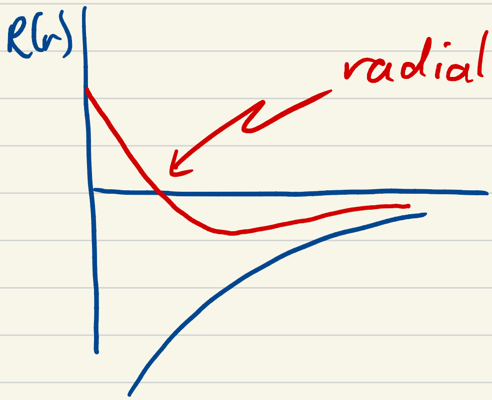
KE scales linearly w/ Z. For heavier elements 1s moves relativistically.

200 "2s"

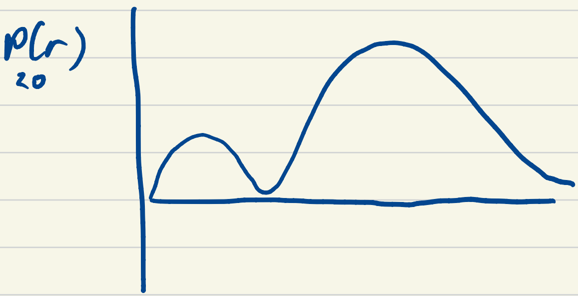
$Y_{00}(\theta, \phi) = \text{constant}$

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

radial node @ $r = 2a_0$

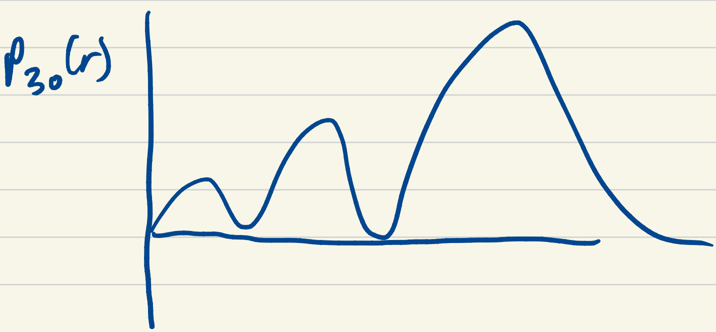


In general, radial node = $n - l - 1$



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

. . .

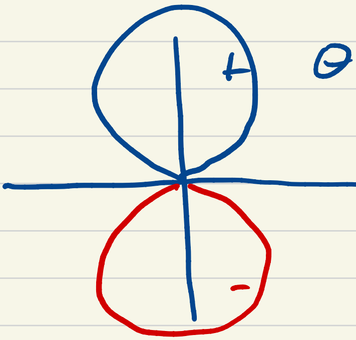


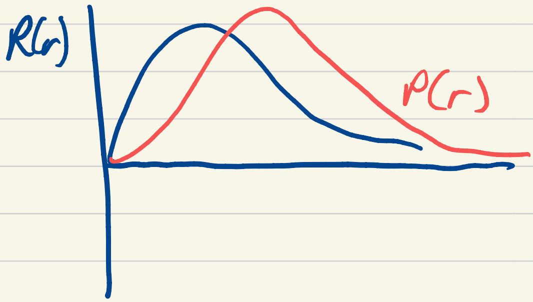
210 "2p"

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

lobe shape

vanishes @ origin





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

More compact on average.

...

d orbitals.

Selection rules

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

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

$$\Delta m_s = 0$$

(emerges from electron conservation of angular momentum)

Example

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

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

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

@ 298 K

Allowed transitions?

$100 \rightarrow 210$

$\rightarrow 310$

$\rightarrow 410$

Fluorescence, Phosphorescence & forbidden transitions