H-atom wavefunction

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\, T_l^m(\theta)\, F_m(\varphi) = R_{nl}(r)\, Y_l^m(\theta,\varphi)$$

n ← principal, l ← azimuthal (orbital), m ← magnetic

$$\psi_{100}(r,\theta,\varphi) = R_{10}(r)\, \underbrace{Y_0^0(\theta,\varphi)}_{\frac{1}{\sqrt{4\pi}}} = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

← 1s state

$$\psi_{100}(x,y,z) = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-\frac{\sqrt{x^2+y^2+z^2}}{a_0}}$$

Normalization $\langle \psi | \psi \rangle = 1$

$$= \int_{\text{All space}} \psi^*_{nlm}(\vec{r})\, \psi_{n'l'm'}(\vec{r})\, dV = 1\, \delta_{nn'}\, \delta_{mm'}\, \delta_{ll'}$$

Probability density $P(\vec{r})$

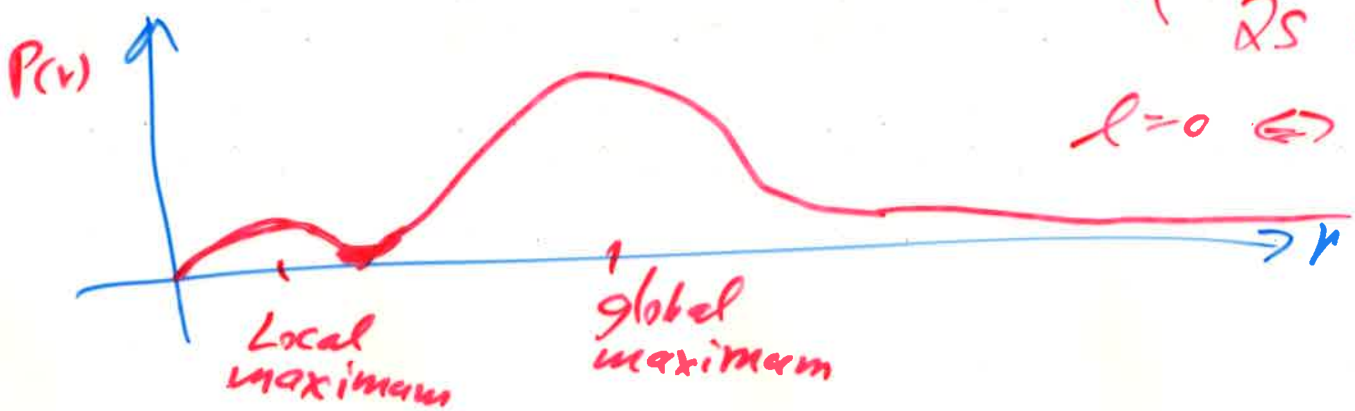
$$= \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \boxed{\psi^*_{nlm}(r,\theta,\varphi)\, \psi_{nlm}(r,\theta,\varphi)\, r^2 \sin\theta}\, dr\, d\theta\, d\varphi$$

$$\int_{x=-\infty}^{+\infty} \int_{y=-\infty}^{+\infty} \int_{z=-\infty}^{\infty} \psi^*_{nlm}(x,y,z)\, \psi_{nlm}(x,y,z)\, dx\, dy\, dz$$

$$\psi_{200}(r,\theta,\varphi) = R_{20}(r)\, Y_0^0(\theta,\varphi) = \frac{1}{4\sqrt{2\pi a_0^3}}\left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}$$

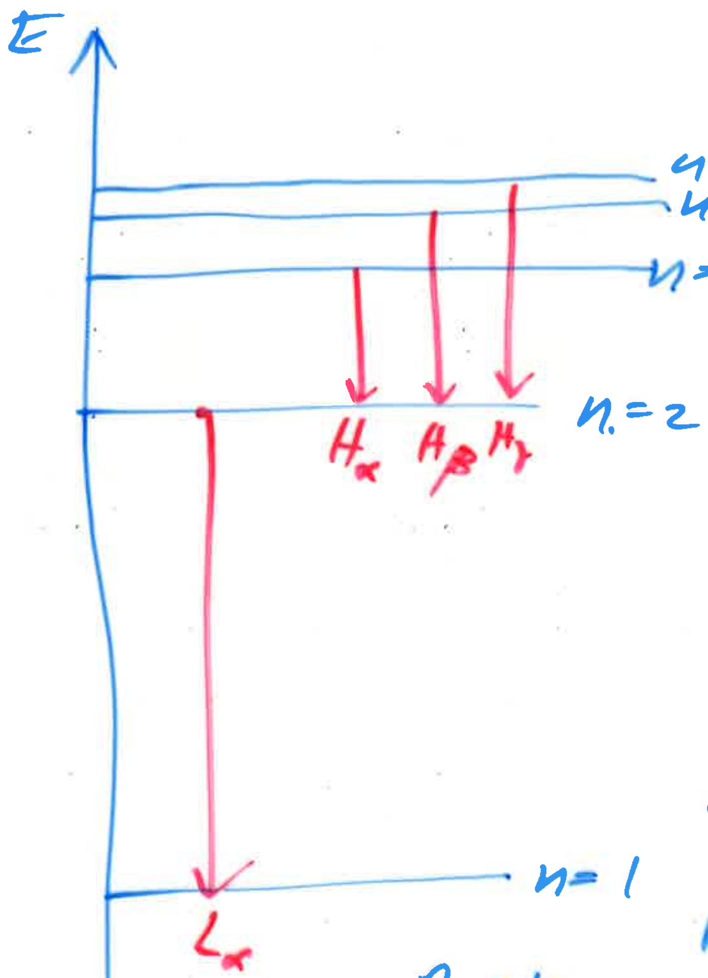
↑ 2s state

$\ell = 0 \Leftrightarrow s$



Spectrum of hydrogen

$$E_n = E_1 \frac{1}{n^2} = (-13.6\,\text{eV}) \frac{1}{n^2}$$



$$E_{photon} = E_i - E_f = E_1\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = \frac{E_1}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$R = 1.097 \times 10^7 \frac{1}{m}$$

Rydberg

Hydrogen β Cyan $n_i = 4$ $n_f = 2$ ← Balmer

$$\frac{1}{\lambda} = \left(1.097 \times 10^{7} \frac{1}{m}\right)\underbrace{\left(\frac{1}{2^2} - \frac{1}{4^2}\right)}_{3/16}$$

$$\lambda = 4.86 \times 10^{-7} m = 4860 \text{Å} = 486 nm$$

Helium and other atoms with more than one electron are <u>very</u> complicated

<u>But</u> Hydrogenic atoms are easy

$Z=2$ He^{+} (2p+2n) in nucleus + 1 electron

$Z=3$ Li^{++}

$Z=29$ $Cu^{+++\ldots++}$

Potential energy $V(r)$

$$\left(\frac{e^2}{4\pi\epsilon_0}\right) \rightarrow \left(\frac{Ze^2}{4\pi\epsilon_0}\right)$$

E_n , a_0

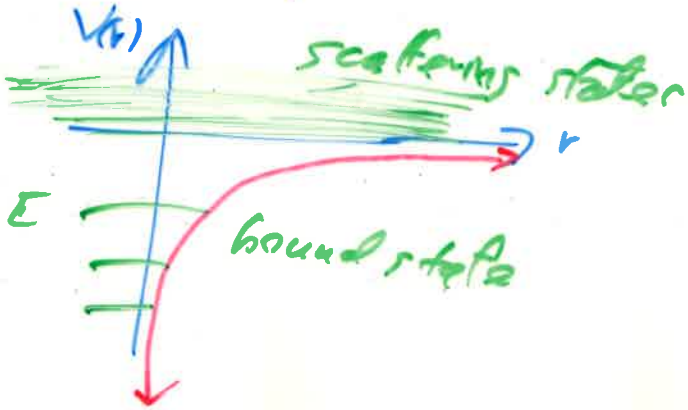
$$m_e \rightarrow \mu = \underbrace{\frac{m_p m_e}{m_p + m_e}}_{0.99946 m_e} \rightarrow \frac{m_N m_e}{m_N + m_e} \approx m_e$$

Nucleus

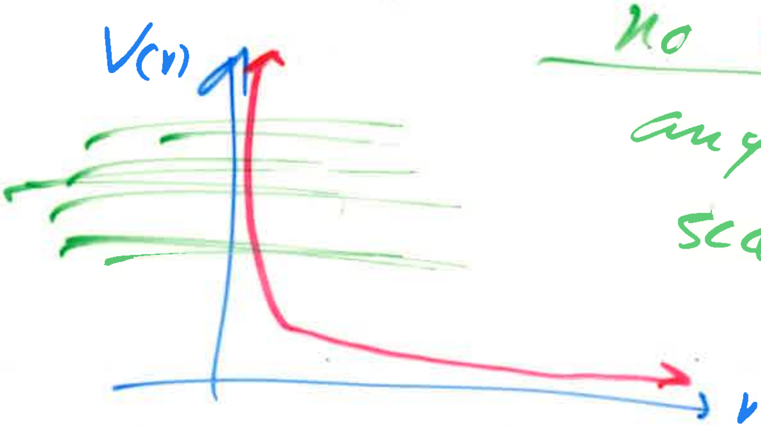
positronium e^+e^-

$\mu = \frac{1}{2} m_e$

If the "nucleus" and the "electron" have opposite charge.



If the "nucleus" and the "electron" have the same charge:



no bound states

any $E > 0$ is ok

scattering states

Angular Momentum

① Orbital ② Spin

Classical Mechanics

$$\boxed{\vec{L} = \vec{r} \times \vec{p}} = \begin{vmatrix} \hat{e}_x & \hat{e}_y & \hat{e}_z \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

Coordinate free

$$\vec{L} = \hat{e}_x \begin{vmatrix} y & z \\ p_y & p_z \end{vmatrix} - \hat{e}_y \begin{vmatrix} x & z \\ p_x & p_z \end{vmatrix} + \hat{e}_z \begin{vmatrix} x & y \\ p_x & p_y \end{vmatrix}$$

$$= \hat{e}_x (y p_z - p_y z) + \hat{e}_y (z p_x - x p_z) + \hat{e}_z (x p_y - y p_x)$$

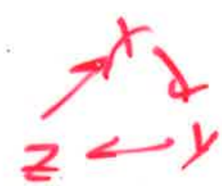
$\rightarrow$ Quantum Mechanics $\quad x \rightarrow \hat{x}$

$$p_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x} = \hat{p}_x$$

$$[\hat{y}, \hat{p}_z] = 0 \Rightarrow \hat{y}\hat{p}_z = \hat{p}_z \hat{y}$$

$$\hat{L}_x = (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)$$

Cyclic permutation



$$\hat{L}_y = (\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)$$

$$\hat{L}_z = (\hat{x}\hat{p}_y - \hat{y}\hat{p}_x)$$

$$[\hat{x}, \hat{p}_x] = i\hbar = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z]$$

$$[\hat{r}_j, \hat{p}_k] = i\hbar \delta_{jk} \qquad [\hat{r}_j, \hat{r}_k] = 0$$

$$[\hat{p}_j, \hat{p}_k] = 0$$

Different components of $\vec{L}$ do not commute

same components $[\hat{L}_x, \hat{L}_x] = 0$

$$[\hat{L}_x, \hat{L}_y] = [(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y), (\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)]$$

$$= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - \underbrace{[\hat{y}\hat{p}_z, \hat{x}\hat{p}_z]}_{0} - \underbrace{[\hat{z}\hat{p}_y, \hat{z}\hat{p}_x]}_{0} + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z]$$

$$= \hat{y}\hat{p}_x \underbrace{[\hat{p}_z, \hat{z}]}_{-i\hbar} + \hat{p}_y\hat{x} \underbrace{[\hat{z}, \hat{p}_z]}_{i\hbar}$$

$$= i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = i\hbar\hat{L}_z$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \Longleftrightarrow [\hat{L}_z, \hat{L}_y] = -i\hbar L_x$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

Consequence $\Rightarrow$ It is impossible to find a state $|\psi\rangle$ which is simultaneously an eigenvector of both $\hat{L}_x$ and $\hat{L}_y$

$$\hat{L}_x|\psi\rangle = \lambda|\psi\rangle \Longrightarrow \hat{L}_y|\psi\rangle \neq \mu|\psi\rangle$$