Polar plots, rotational spectroscopy, and an introduction to the hydrogen atom

Note Title 03-11-2009

Reminder:

Quiz tomorrow: Usual venue at 1715 hrs.

harmonic oscillator.

1) What is the energy of a rotor if it is found in the state

$$(5\cos^2\theta - 1)\sin\theta \; ?$$

2) What is the z-component of the angular momentum in this state?

3) What is the result of operating on this state with

$$-\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

Energies of a rigid roter

$$E = \frac{l(l+1)\hbar^2}{2I} = \frac{J(J+1)\hbar^2}{2I}$$

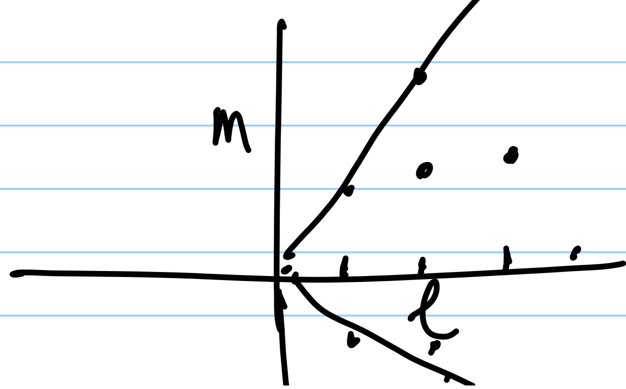
$l = 0, 1, 2, \ldots$

$l \equiv J$

$m = -l$ to $+l$ in integer steps

$\psi = Y_{lm}$ (spherical harmonics)

$$= \underbrace{P_{lm}(\cos\theta)} \times e^{im\varphi}$$



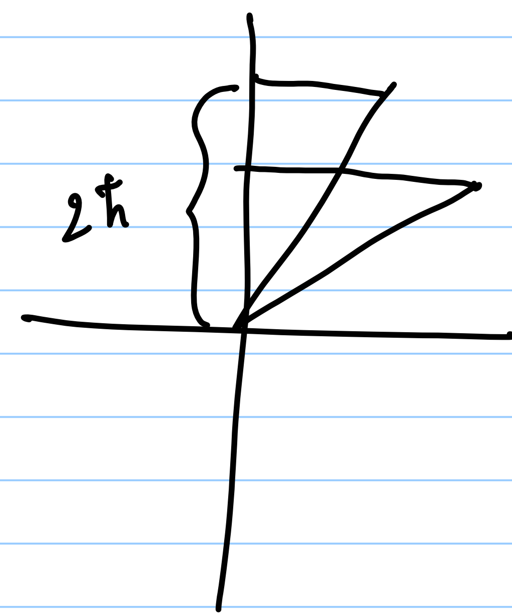
Space quantization

$$[L_x, L_y] = i\hbar L_z$$

L^2 and L_z

x, y components are undefined

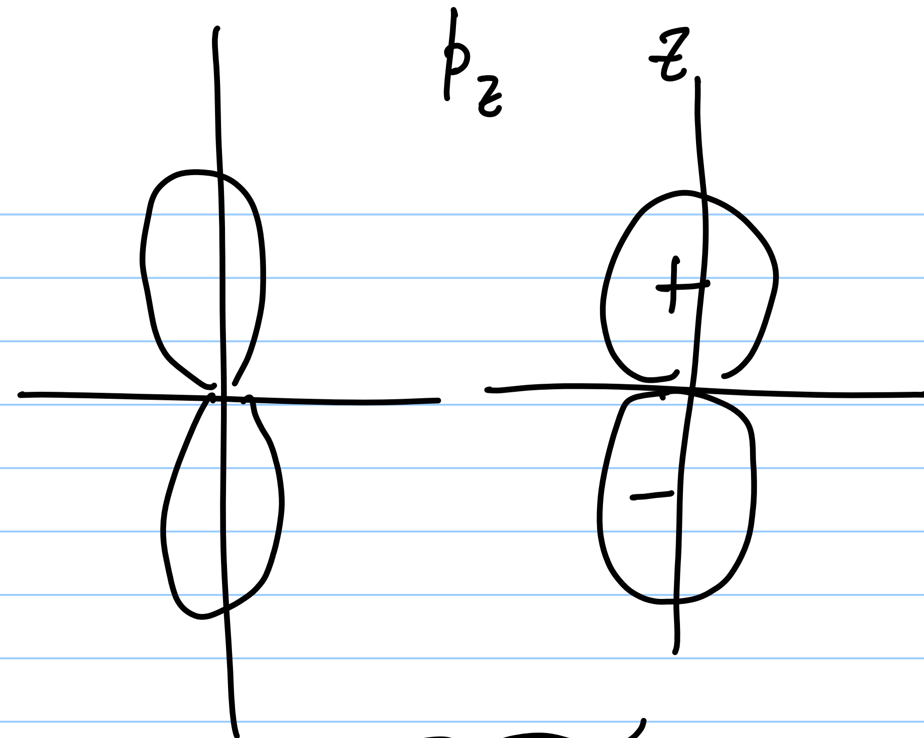
$2\hbar$



$$\psi_{p_z} = Y_{10}$$

$$= P_{10}(\cos\theta) \times 1$$

$$= \cos\theta$$

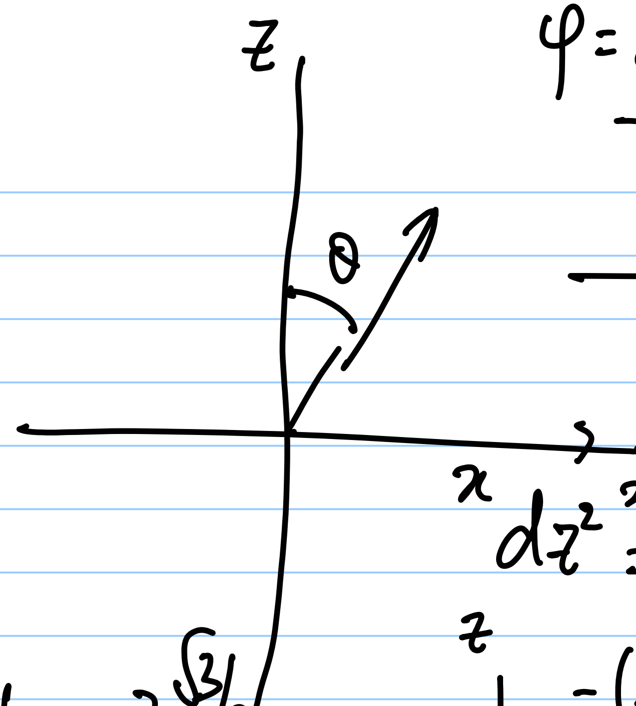


Polar plots

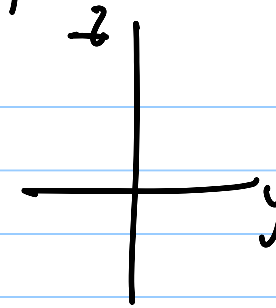
$$\psi^* \psi \, d\tau$$

$\varphi = 0$

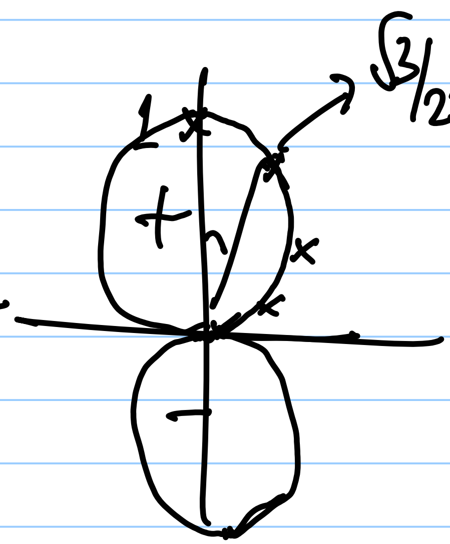
θ	$\cos\theta$
0	1
30	$\sqrt{3}/2$
45	$\frac{1}{\sqrt{2}}$
60	$\frac{1}{2}$
90	0



$\varphi = 90°$

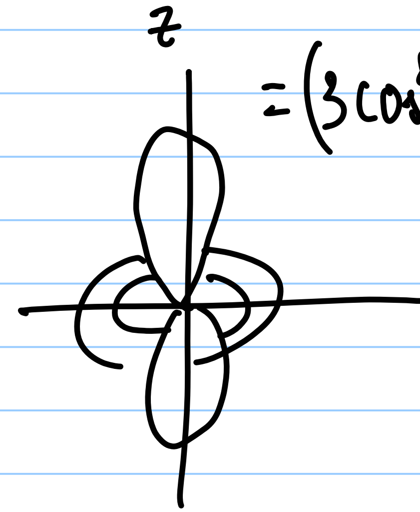


$|\psi|^2$



$d_{z^2} = Y_{20}$

$= (3\cos^2\theta - 1) \times 1$



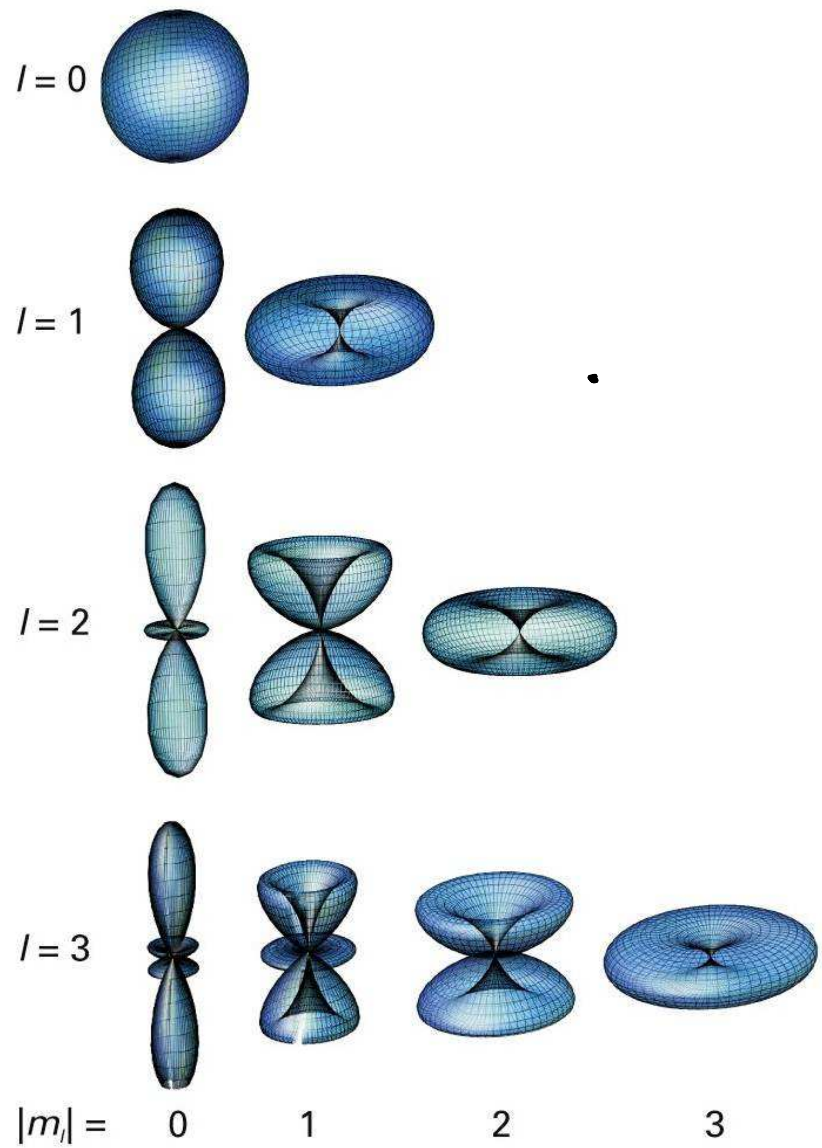
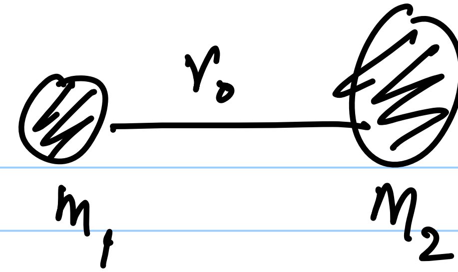
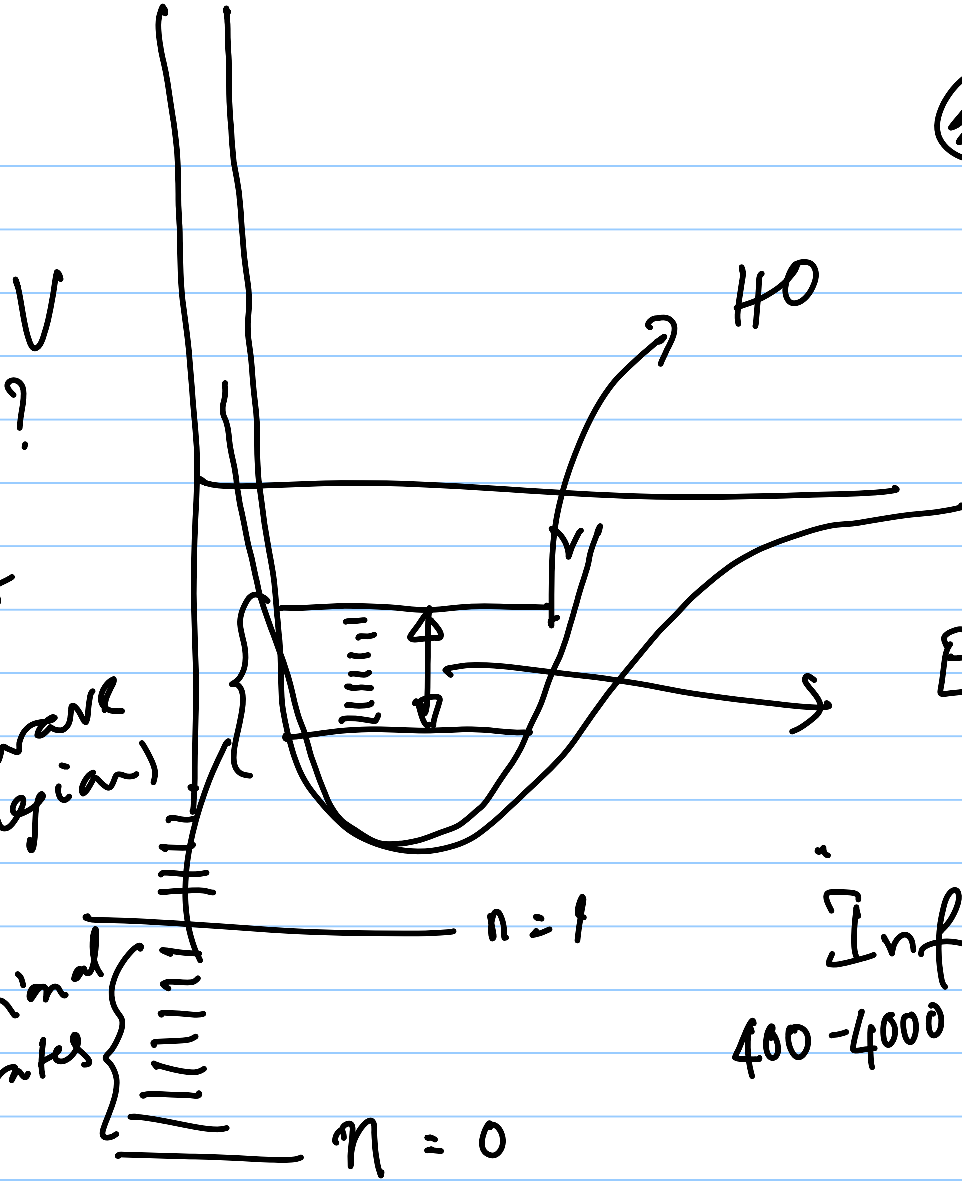


Figure 9-37
Atkins Physical Chemistry, Eighth Edition





$n=1, \ l=?$

ψ_{rot}

ψ_{vib}

p

(microwave region)

$E_n = (n+\frac{1}{2})\hbar\omega$

$\omega = \sqrt{\frac{k}{\mu}}$

"Infra red region"

400-4000 cm^{-1}

$$E_{rot} = \frac{l(l+1)\hbar^2}{2I} \quad l(l+1) \to (2l+1)$$

$I = \mu r^2$

μ: reduced mass

$l = 1$ state

$l = 2$

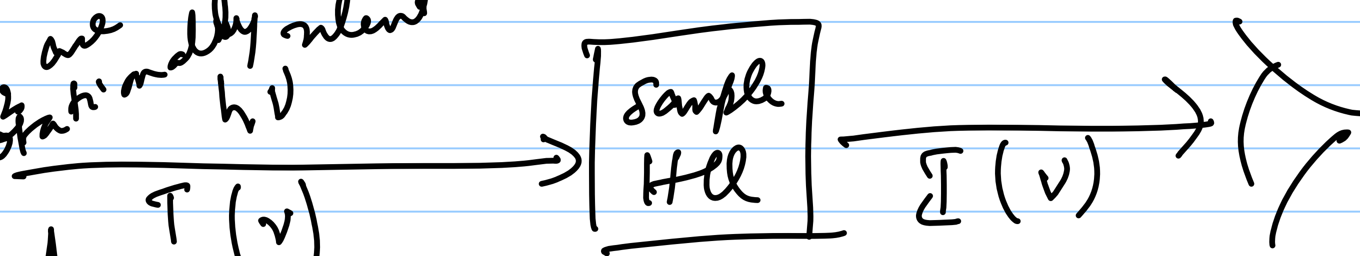
$\frac{6\hbar^2}{2I}$

$\frac{2\hbar^2}{2I}$

$E_0 = 0$

1) Molecule must have a permanent dipole moment

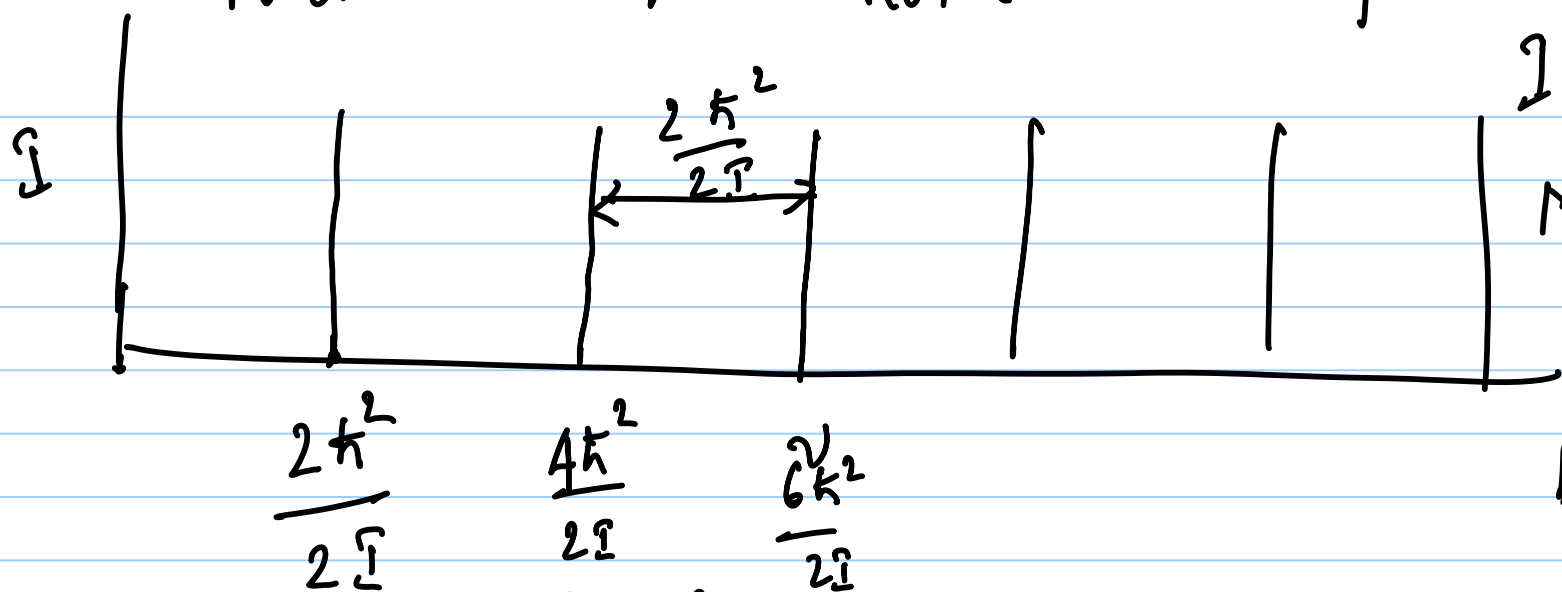
N_2, O_2 are rotationally silent



2) $\Delta l = \pm 1$

"Microwave region" Rotational spectrum

$I = \mu r^2$



Measure of $r \rightarrow$ bond distance

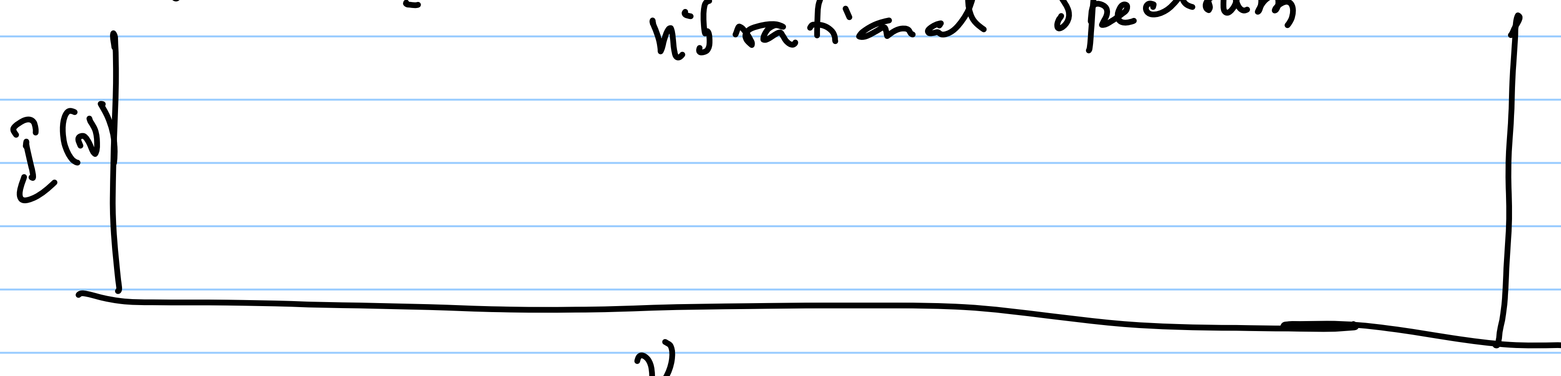
$l=1 \rightarrow l=2$

$l=0 \rightarrow l=1$

$l=2 \rightarrow l=3$

Vibrational Spectrum

$\hbar\omega$



Hydrogen atom

H, He^+, hydrogenic

Ze^2 r e

$$\hat{H} = \left(-\cancel{\frac{\hbar^2}{2m_N}\nabla_N^2} - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{Ze^2}{r}\right)$$ proton

Nuclear kinetic energy ≈ 0

$$\hat{H}\psi = E\,\psi(\vec{r}_e, \vec{r}_N)$$

nucleus ~ 2000 times heavier than the electron

Nucl

$$\frac{1}{\mu} = \frac{1}{m_N} + \frac{1}{m_e} \approx \frac{1}{m_e}$$

"Conservation of Angular momentum"

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\psi = E\psi$$

$$\nabla^2 = \left\{\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \underbrace{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}}_{\to L^2}\right\}$$

$$\left\{-\frac{\hbar^2}{2m}\left\{\quad\right\} - \frac{Ze^2}{r}\right\}\psi = E\psi$$

$$\psi = R(r)\,\Theta(\theta)\,\Phi(\varphi)$$

$$\mathcal{H}\psi = E\psi$$

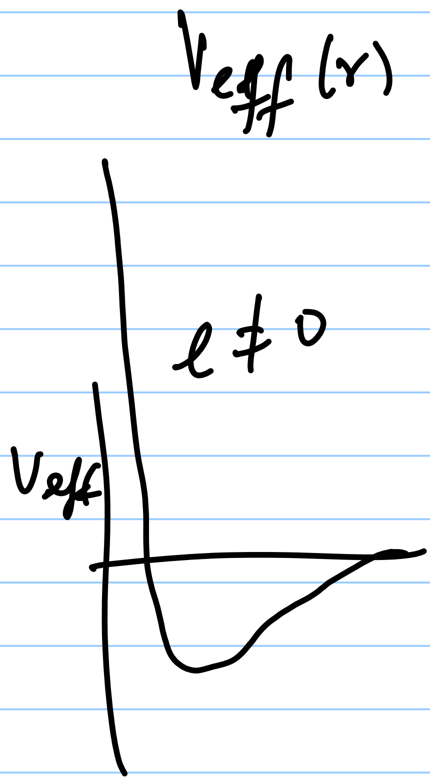
$$L^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$$

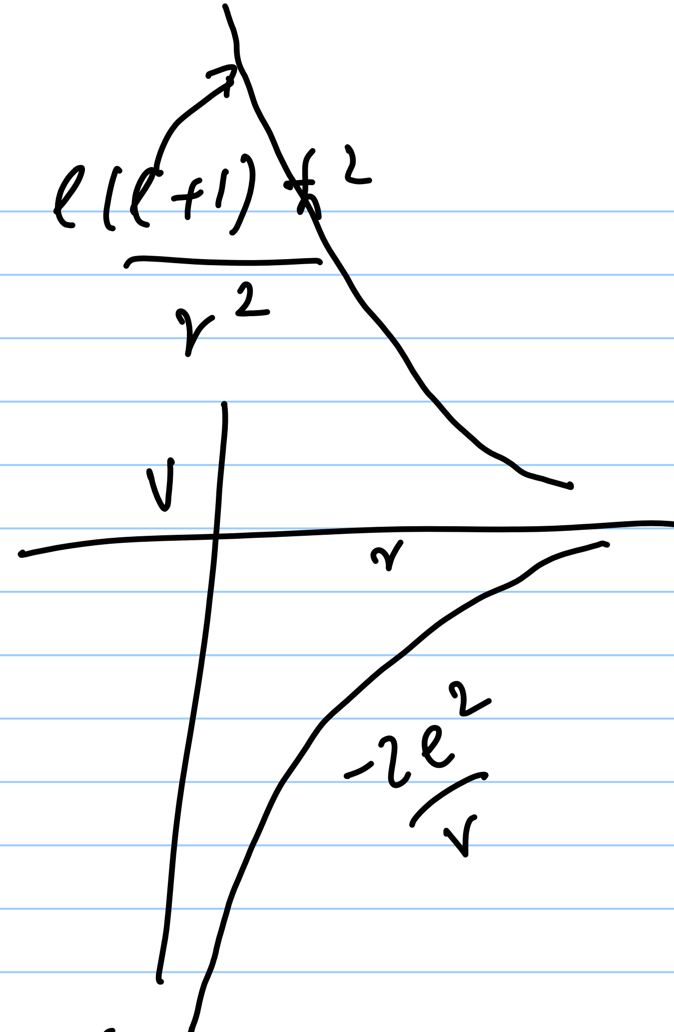
$$\left\{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r^2} + \frac{1}{r^2}\left\{L^2 \quad \right\}\right\} R(r)\,Y_{lm}$$

$$-\frac{Ze^2}{r}$$

"s" states

$$V_{eff} : -\frac{Ze^2}{r} + \frac{l(l+1)\hbar^2}{r^2}$$





$R(r) \to 0$ as $r \to 0$
for $l \neq 0$

Wave function of the spherically symmetric ground state $(\ell = 0)$

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Ze^2}{r}$$

$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) = 2r\frac{\partial}{\partial r} + r^2\frac{\partial^2}{\partial r^2}$$

$$\hat{\mathcal{H}} R = E R$$

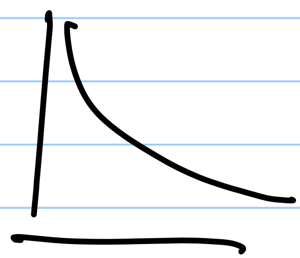
$$\left\{-\frac{\hbar^2}{2m}\frac{1}{r^2}\underbrace{\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}} - \frac{Ze^2}{r}\right\} R = E R \quad \text{—} \; 1$$

$$\left\{-\frac{\hbar^2}{2m}\frac{1}{r^2}\left(2r\frac{\partial}{\partial r} + r^2\frac{\partial^2}{\partial r^2}\right) - \frac{Ze^2}{r}\right\} R = E R$$

For $r \to \infty$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}R = ER$$

$$\psi = Ae^{\pm\alpha r} \qquad \alpha = -\sqrt{\frac{2mE}{\hbar^2}}$$

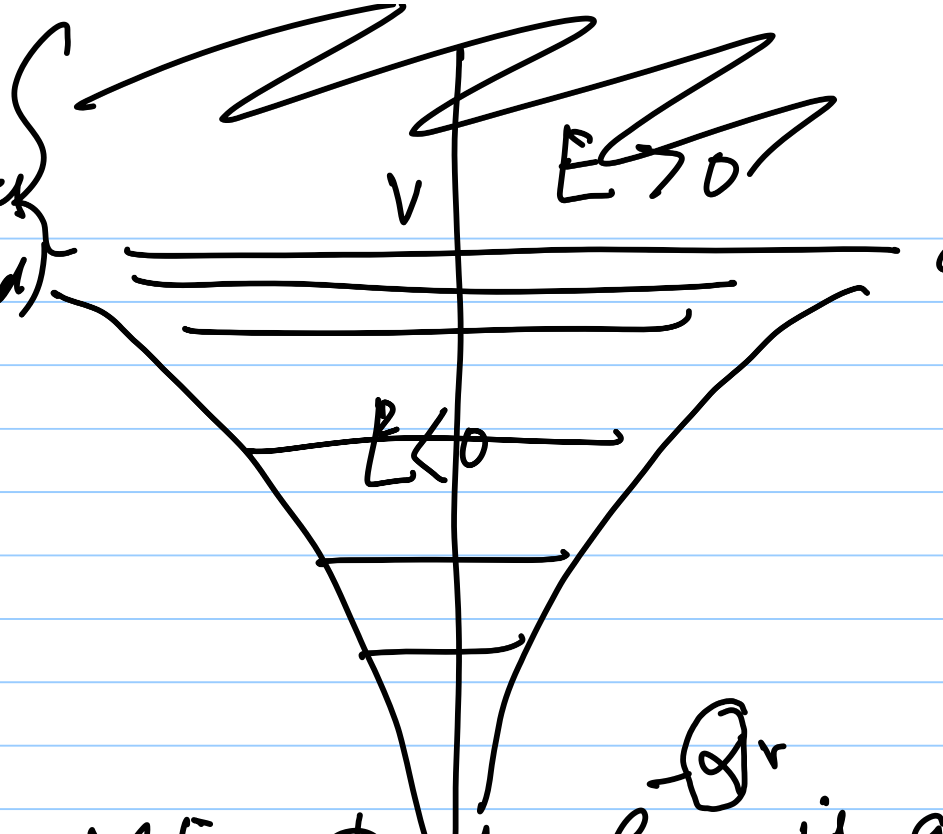


$$\psi(r\to\infty) = Ae^{-\alpha r}$$

Scattering states

"Not bound"

$e^{ik(r)\cdot r}$



ASS U ME that $e^{-\alpha r}$ is a solution for all "r"

$$R(r) = e^{-\alpha r}$$

No nodes either in the angular & radial

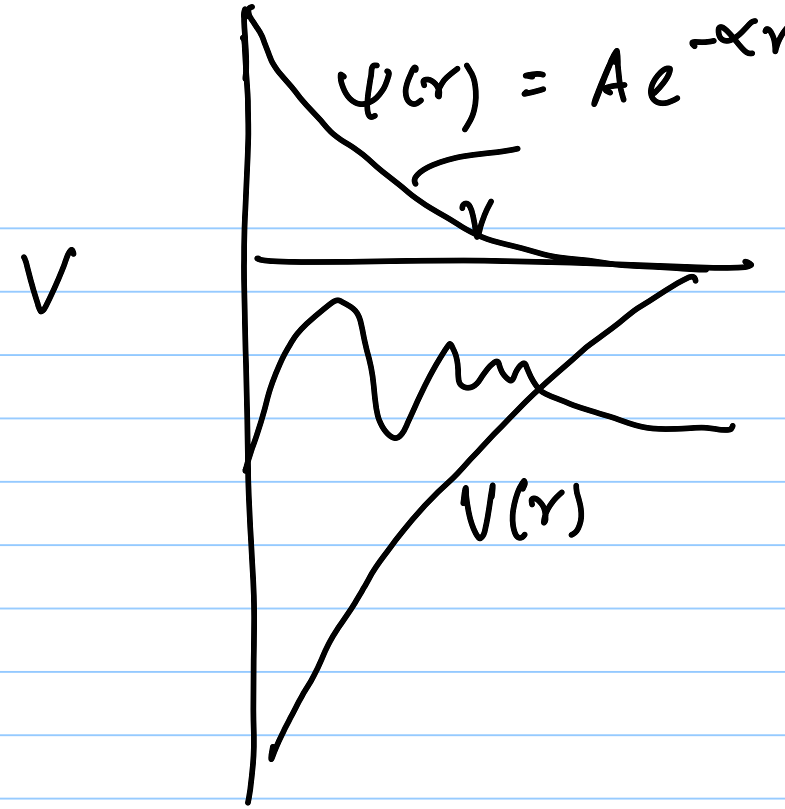
$$\left\{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}-\frac{Ze^2}{r}\right\}Ae^{-\alpha r}=EAe^{-\alpha r}$$

$\vdots$

$$\left(\underbrace{\begin{matrix}\text{two term}\\ \text{Constant}\\ \alpha, E\end{matrix}}\right)+f(r)\left(\underbrace{\begin{matrix}\text{diff}\\ \text{two term}\\ \text{constant}\\ \alpha, E\end{matrix}}\right)=0$$

condition for α

independently have to be zero


$\psi(r) = Ae^{-\alpha r}$
r
V
$V(r)$