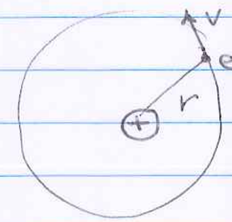
Central potential $U(\vec{r}) = U(r)$

spherically symmetric

Coulumb potential:



$U(r) = -\dfrac{ke^2}{r}$

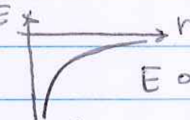
$k = \dfrac{1}{4\pi\varepsilon_0}$

also gravity

Classical motion: circular orbits $\dfrac{mv^2}{r} = \dfrac{ke^2}{r^2} \Rightarrow mv^2 r = ke^2$

Planets move in closed orbits $\longrightarrow$ bound state
(classically) (quantum)

$E = \frac{1}{2}mv^2 - \frac{ke^2}{r} = -\frac{1}{2}\frac{ke^2}{r}$

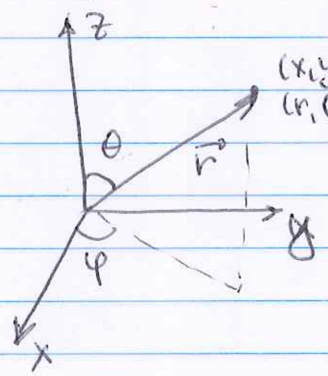


$E \propto 1/r$

However, now we cannot separate the motion into independent 1D pieces in Cartesian coordinates! $r = \sqrt{x^2+y^2+z^2}$, they are not independent

Since potential is spherically symmetric, and classically we expect circular motion, it make sense to switch to spherical coordinates

$(x, y, z) \longrightarrow (r, \theta, \varphi)$



$r = \sqrt{x^2+y^2+z^2}$

$z = r\cos\theta$

$x = r\sin\theta\cos\varphi$

$y = r\sin\theta\sin\varphi$

Schrodinger equation for the Coulumb potential

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{\overset{=1 \text{ for now}}{Z}\, e^2}{4\pi\varepsilon_0}\frac{1}{r}\psi = E\psi$$

In spherical coordinates $\psi(r,\theta,\varphi)$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(r,\theta,\varphi)}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\left[\frac{\partial^2\psi}{\partial\theta^2} + \cot\theta\frac{\partial\psi}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right]\right)$$
$$-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\psi = E\psi$$

One can show that any solution of this equation can be written as

$$\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi)$$

where $Y_{\ell m}(\theta,\varphi)$ is the solution of

$$\frac{\partial^2 Y_{\ell m}}{\partial\theta^2} + \cot\frac{\partial Y_{\ell m}}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y_{\ell m}}{\partial\varphi^2} = -\ell(\ell+1)Y_{\ell m}$$

$$Y_{\ell m}(\theta,\varphi) = \underbrace{P_{\ell m}}_{\substack{\text{Legandre}\\ \text{polynomials}}}(\cos\theta)\, e^{im\varphi} \quad \text{— spherical functions}$$

Spherical functions describe angular dependence of any eigen wave function in a spherically symmetric potential (and any angular dependence of a regular wave in a 3D spherical cavity)

One can show mathematically that $Y_{\ell m}(\theta,\varphi)$ exists only if $\ell = 0, 1, 2 \ldots$

$$m = \underbrace{0, \pm1, \pm2, \ldots \pm\ell}_{\substack{2\ell+1 \text{ possible}\\ \text{values for any } \ell}}$$

One can also show that for the coulumb potential

$n = 1, 2 \ldots$

$\ell = 0, 1, \ldots n-1$

Shockingly, the energy of a state <u>does not</u> depend on either ℓ or m, only on n!

& Electron stationary states: orbitals

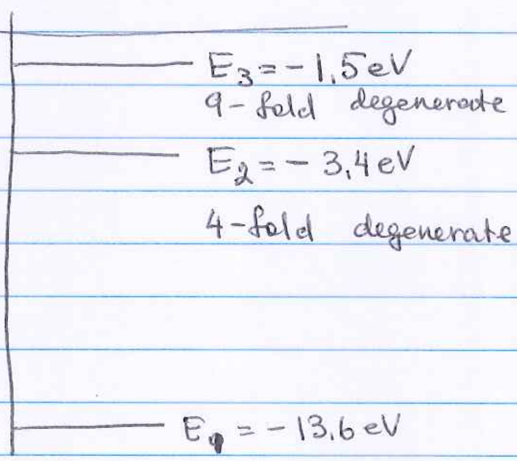
(n, ℓ, m) $\quad E_n = -\dfrac{ke^2}{2a_0}\dfrac{1}{n^2} = -\dfrac{E_R}{n^2}$

$E_R = 13.6\,eV$ Rydberg energy

$a_0 = \dfrac{\hbar^2}{mke^2}$ – Bohr radius, $a_0 \approx 0.5 \cdot 10^{-10}\,m$

Average orbit size $r_n \sim n a_0$
(the large is n, the larger is the orbit radius)

Notice, that all excited electronic states of H-atom are highly degenerate



Ground state $n=1$
$E_1 = -E_R$ $\quad \ell = 0, m = 0$

First excited state $n=2$
$E_2 = -E_R/4$ $\quad \ell = 0, m = 0$
$\ell = 1, m = 0, \pm 1$

Second excited state $n=3$
$E_3 = -E_R/9$ $\quad \ell = 0 \quad m = 0$
$\ell = 1, m = 0, \pm 1$
$\ell = 2, m = 0, \pm 1, \pm 2$

For each n: $\ell = 0, 1 \dots n-1$ – n different states
$\hookrightarrow$ for each ℓ; $m = 0, \pm 1, \dots \pm \ell$ $\quad (2\ell+1)$ states

Total degeneracy for n! $\quad 1 + 3 + 5 + \dots [2(n-1)+1] = n^2$
Each n state is n^2-fold degenerate

Quantum Numbers n	l	m_l	Eigenfunctions
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos \theta$
2	1	± 1	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin \theta \, e^{\pm i\varphi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \cos \theta$
3	1	± 1	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \sin \theta \, e^{\pm i\varphi}$