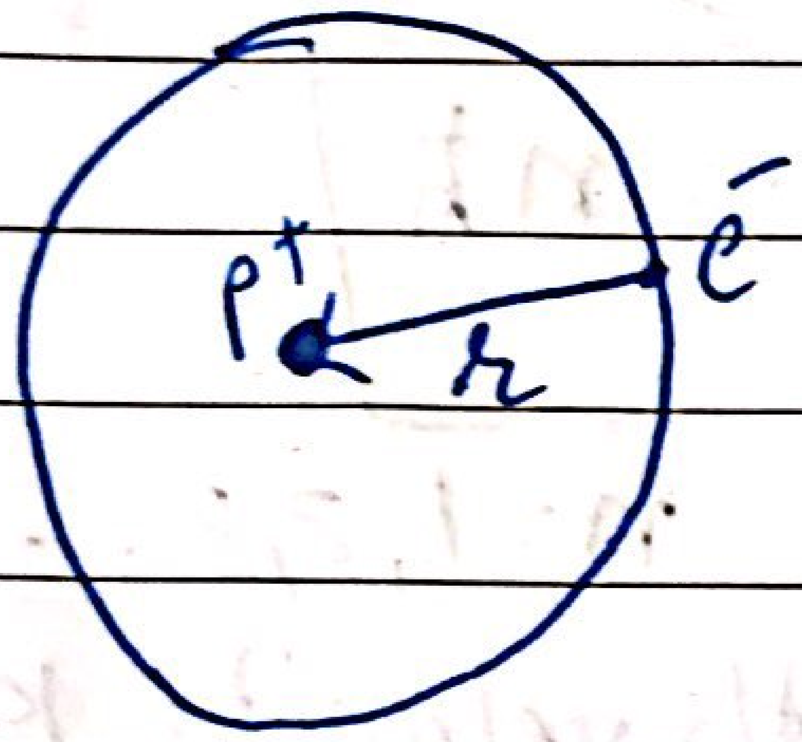
☆ Schrodinger Wave Equation to the Hydrogen Atom

→ The potential energy of the electron-Proton system is electrostatic

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



(−)ve sign shows bounded electron

e – charge of electron

ϵ_0 → Permittivity of free space

r → radius of H-atom

→ three dimensional time-independent Schrodinger equation:

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x,y,z)}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right]$$

$$= E - V(r) \longrightarrow (1)$$

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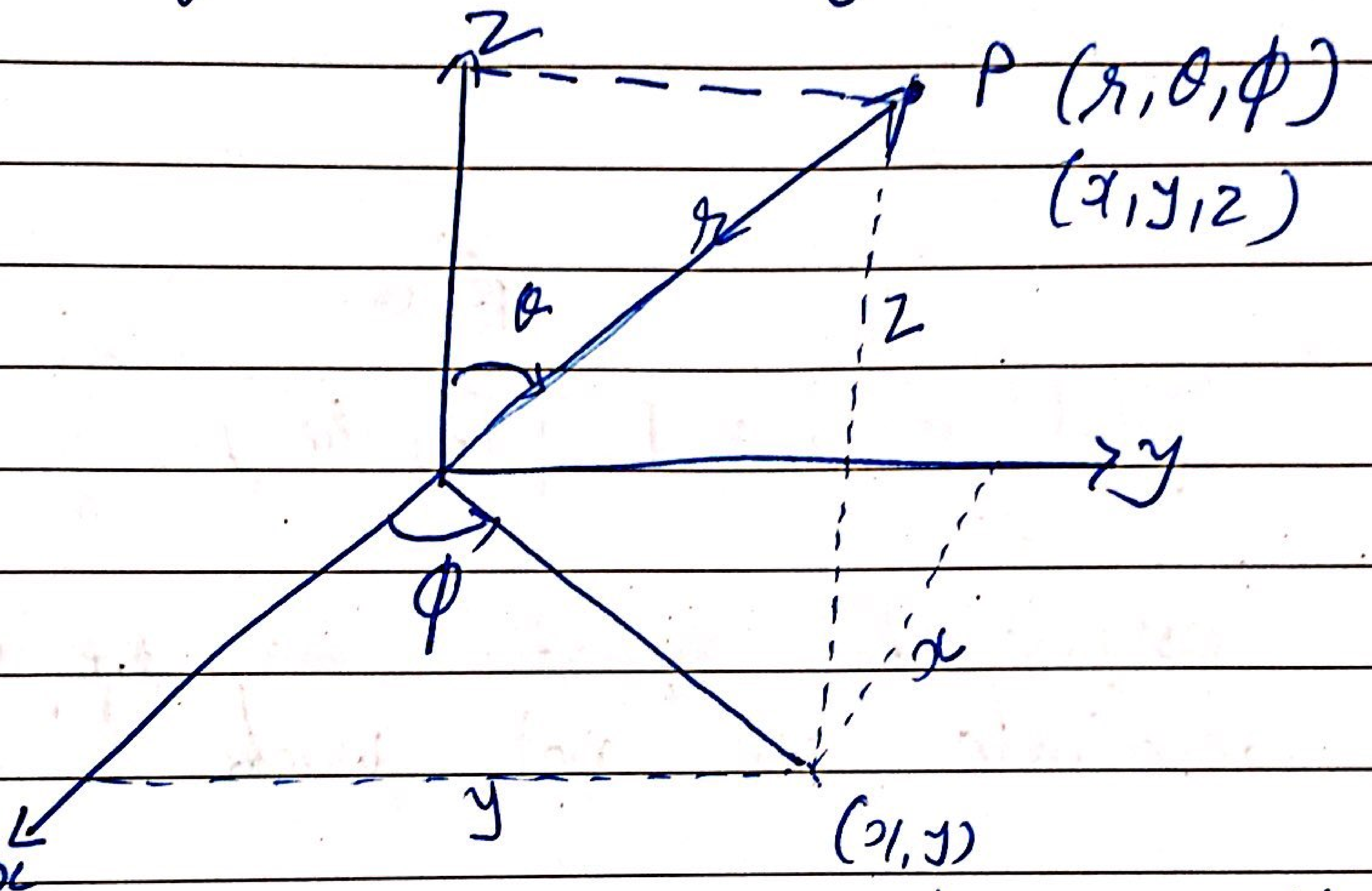
for Hydrogen like atoms (He^{+} or Li^{++})

→ Replace e^2 with Ze^2 (Z → atomic number)

→ Use reduced mass → μ

→

for easy solving convert into Polar spherical Coordinate because of the radial symmetry.



Length of the radius vector

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

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

$y = r \sin\theta \sin\phi$

$z = r \cos\theta$ → $\theta = \cos^{-1}\left(\frac{z}{r}\right)$ (Polar angle)

$\frac{x}{y} = \frac{\cancel{r \sin\theta}}{\cancel{r \sin\theta}} \frac{\cos\phi}{\sin\phi} = \tan\phi = y/x$

$= \phi = \tan^{-1}(y/x)$ (Azimuthal angle)

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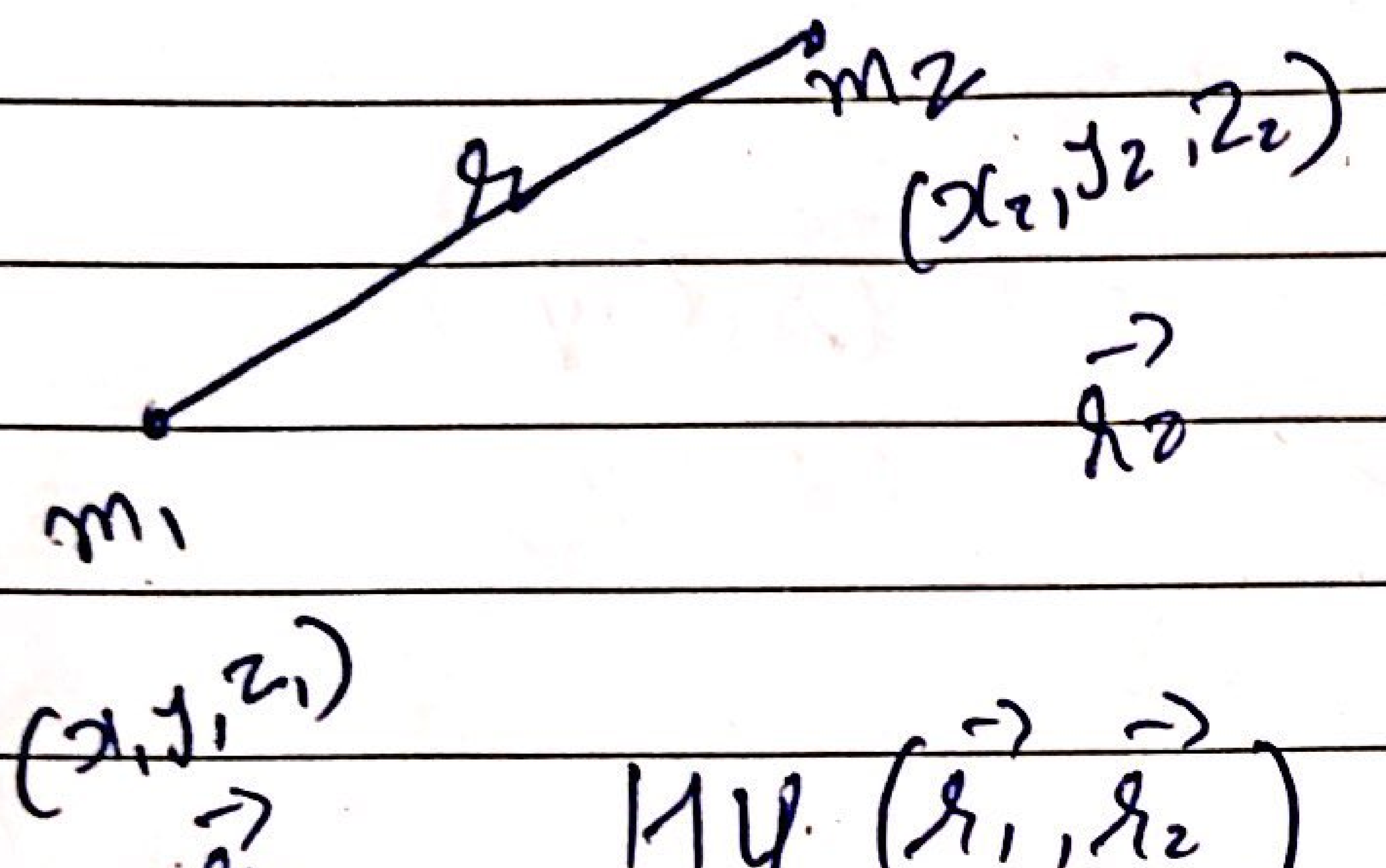
Now, We can re-write Schrodinger equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0.$$

$V(r)$



$\vec{R}$

$$H\psi(\vec{r_1}, \vec{r_2}) = E\psi(\vec{r_1}, \vec{r_2})$$

$\downarrow$

If We assume this equation so separation of coordinate will not work.

So, We will introduce two coordinates here.

1) Center of mass coordinate

$$\vec{R} = \frac{m_1\vec{r_1} + m_2\vec{r_2}}{m_1 + m_2}$$

Relative coordinate $\vec{r} = \vec{r_1} - \vec{r_2}$

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Hamiltonian Operator

$$H = \frac{-\hbar^2}{2M}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$$

$(M = m_1 + m_2)$

$$- \frac{\hbar^2}{2\mu}\left[\nabla^2\right] + V(r)$$

$\nabla^2 = \partial^2/\partial x^2 + \dots + \partial^2/\partial z^2$

Schrodinger Equation

$$H\,\psi(\vec{R}, \vec{r}) = E\,\psi(\vec{R}, \vec{r})$$

assume,

$$\psi(\vec{R}, \vec{r}) = \phi(\vec{R}) \cdot \psi(\vec{r})$$

here, Method of speration will work here.

Reduced mass

$$\left[\; \mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \;\right]$$

$\phi(\vec{R}) \rightarrow$ free translational motion of center of mass

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Free translation motion of the Center of Mass

Solution of $\phi(\vec{R})$

$$\phi(\vec{R}) = e^{i\vec{P}\cdot\vec{R}/\hbar} \qquad \left(\frac{P^2}{2M} = E_c\right)$$

Schroding eqn

$$\nabla^2\psi + \frac{2\mu}{\hbar^2}\left[E - V(r)\right]\psi(r,\theta,\phi) = 0$$

$$\left(\vec{r} = \vec{r}_1 - \vec{r}_2\right)$$

Two particle problem can be reduced to two parts

1. → Free translational motion of the center of Mass
2. → Internal motion of the two particles

Which satisfies the spherically symmetric potential energy Shrodinger equation.

→ Mass is replaced by reduced mass μ
→ Correct Solution for any two particle system.

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$

Angular Momentum operator

$$L^2\psi = \left(L_x^2 + L_y^2 + L_z^2\right)\psi$$

$$= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$

Which is similar to last two step of above equation

So, Sch. Eq^n will be

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{L^2\psi}{r^2\hbar^2} + \frac{2\mu}{\hbar^2}\left[E - V(r)\right]$$

$$\psi(r,\theta,\phi) = 0.$$

Potential energy does not depend on θ & ϕ only on $\vec{r}$ → ~~called~~

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Such a potential energy is called Spherically Symmetric Potential.

Using method of Seperation of variables

$$\psi(r,\theta,\phi) = R(r)\, Y(\theta,\phi)$$

$$\frac{Y(\theta,\phi)}{r^2}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \frac{2\mu}{\hbar^2}\left[\varepsilon - V(r)\right] R(r) Y$$

$$= R(r)\frac{L^2 Y}{r^2\hbar^2}$$

multiplying whole eq^n by

$$\frac{r^2}{R(r)\, Y(\theta,\phi)}$$

$$\frac{1}{R}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \frac{2\mu r^2}{\hbar^2}\left[\varepsilon - V(r)\right]$$

$$= \frac{L^2 Y(\theta,\phi)}{\hbar^2 Y(\theta,\phi)} = \lambda$$

L.H.S. $\rightarrow f(r)$

R.H.S. $\rightarrow$ function of (θ,ϕ).

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$\mathcal{S}_1,\quad L^2 Y(\theta,\phi) = \lambda \hbar^2 Y(\theta,\phi)$

This eq^n gives eigenvalues & eigen function of the operator L^2

where, $\lambda = l(l+1)$; $l = 0,1,2,3\ldots$
from this value eq^n is satisfied

$Y(\theta,\phi) = Y_{lm}(\theta,\phi) = m = -l, 0, +l$

$\downarrow$

spherical harmonics

$Y_{lm}(\theta,\phi) = F(\theta)\,\dfrac{1}{\sqrt{2\pi}}\,e^{im\phi}$

$\downarrow$

simultaneous function of L^2 & L_z

$L_z Y_{lm}(\theta,\phi) = L_z\, F(\theta)\,\dfrac{1}{\sqrt{2\pi}}\,e^{im\phi}$

as We know that $L_z = -i\hbar \dfrac{\partial}{\partial\phi}$

$L_z Y_{lm}(\theta,\phi) = m\hbar\, Y_{lm}(\theta,\phi)$

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$Y_{lm}(\theta, \phi) \rightarrow$ are simultaneous eigen functions of the operator L^2 & L_z

$$Y_{l0} = \sqrt{\frac{2l+1}{2}}\, P_l(\cos\theta) \cdot \frac{1}{\sqrt{2\pi}} \qquad (m=0)$$

from Eqn:

Radial Part of equation

$$\frac{1}{R}\frac{d}{dr}\left[r^2 \frac{dR}{dr}\right] + \frac{2\mu r^2}{\hbar^2}\left[\mathcal{E} - V(r)\right] - \lambda = 0$$

$$(\lambda = l(l+1))$$

$$\frac{1}{R}\frac{d}{dr}\left[r^2 \frac{dR}{dr}\right] + \frac{2\mu r^2}{\hbar^2}\left[\mathcal{E} - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2}\right] = 0$$

multiplying with $\frac{R(r)}{r^2}$

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2 \frac{dR}{dr}\right] + \frac{2\mu}{\hbar^2}\left[\mathcal{E} - V(r) - \frac{l(l+1)\hbar^2}{2\mu r^2}\right] R(r)$$

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Atomic/Molecular Physics & Spectroscopy

Course: M.Sc. Physics

Semester – II

Prepared by

Dr. Manisha Vithalpura

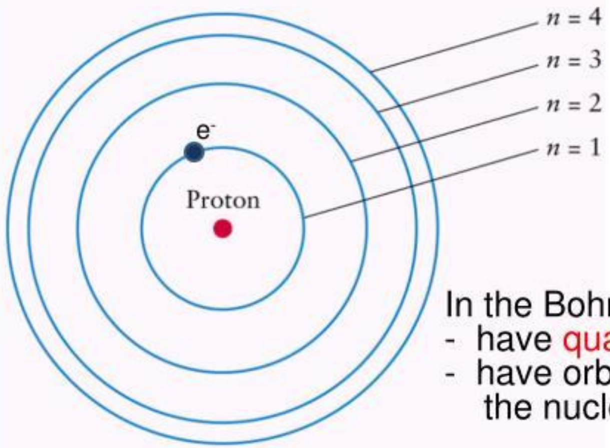
Assistant Professor

Department of Physics

ISHLS

Indus University

Bohr Model of Hydrogen Atom



In the Bohr model, electrons:
- have quantized energies.
- have orbits a fixed distance from the nucleus.

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Postulates of Bohr Model of the H Atom

- Bohr's first postulate was that each atom has certain definite stable states in which it can exist, and each possible state has definite total energy. These are called the stationary states of the atom.

- Bohr's second postulate defines these stable orbits. This postulate states that the electron revolves around the nucleus only in those orbits for which the angular momentum is some integral multiple of $h/2\pi$ where h is the Planck's constant ($= 6.6 \times 10–34$ J s). Thus the angular momentum (L) of the orbiting electron is quantised. That is, $L_n = nh/2\pi$.

- The electrons present in an atom can move from a lower energy level (E_{lower}) to a level of higher energy (E_{higher}) by absorbing the appropriate energy. Similarly, an electron can jump from a higher energy level (E_{higher}) to a lower energy level (E_{lower}) by losing the appropriate energy.

  The energy absorbed or lost is equal to the difference between the energies of the two energy levels, i.e.,

$$\Delta E = E_{higher} - E_{lower}$$

https://youtu.be/KvCezk9DJfk

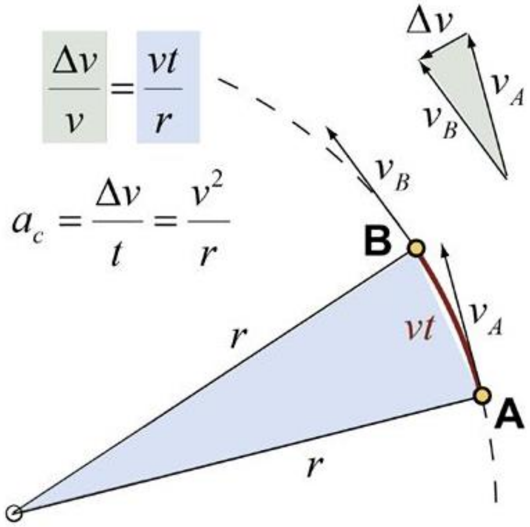
Centripetal Force Equation

Combining these two equations . . .

$$F_c = ma_c \quad \text{and} \quad a_c = \frac{v^2}{r}$$

you get:

$$F_c = \frac{mv^2}{r}$$

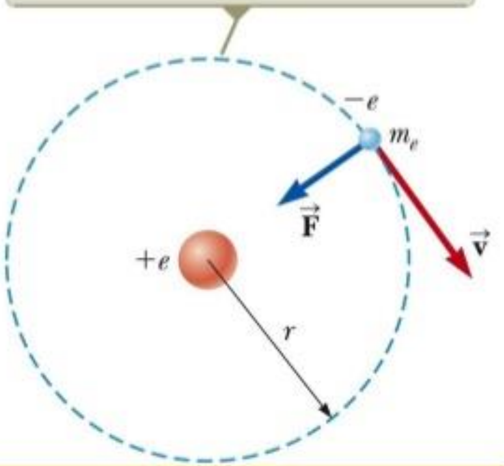


Bohr's Postulates for Hydrogen, 1

The electron moves in circular orbits around the proton under the electric force of attraction.

- The Coulomb force produces the centripetal acceleration.

The orbiting electron is allowed to be only in specific orbits of discrete radii.



2^{nd} Postulate : mvr=nh/2π

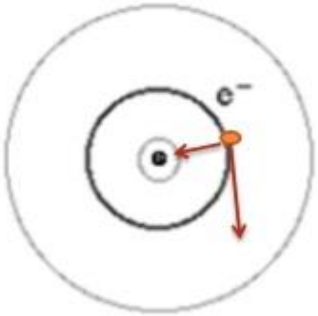
$$\therefore \quad \frac{mv^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2}$$

$$\therefore \quad mv^2 = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

$$\therefore \quad \frac{1}{2}mv^2 = \frac{1}{2} \times \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

$$\therefore \quad \text{Kinetic energy of electron} = \frac{e^2}{8\pi\varepsilon_0 r}$$

THE ENERGIES OF ORBITALS



There are 2 forces acting on a circling electron:

- Electrostatic attraction
- Centripetal force

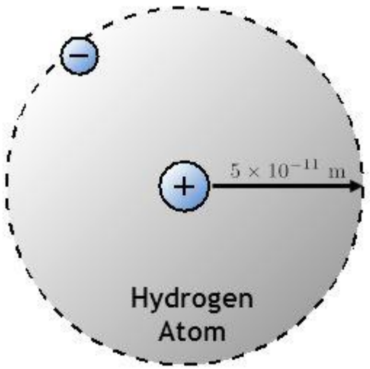
They must be equal to keep the electron stable:

$$F = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2} = \frac{m_e v^2}{r}.$$

The kinetic energy is then: $\boxed{\frac{1}{2}m_e v^2 = \frac{1}{8\pi\epsilon_0}\frac{e^2}{r}}$

Consider a single hydrogen atom:

an electron of *charge* = -*e* free to move around
in the electric field of a fixed proton of *charge* = +*e*
(proton is ~2000 times heavier than electron, so we
consider it fixed).



The electron has a potential energy due to the attraction to proton of:

$$V(r) = -\frac{e^2}{4\pi\epsilon_o r}$$ where r is the electron-proton separation

The electron has a kinetic energy of $$K.E. = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

The total energy is then $$E(r) = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_o r}$$

$$\therefore \text{ Total energy of electron } = \frac{e^2}{8\pi\varepsilon_0 r} + \frac{-e^2}{4\pi\varepsilon_0 r}$$

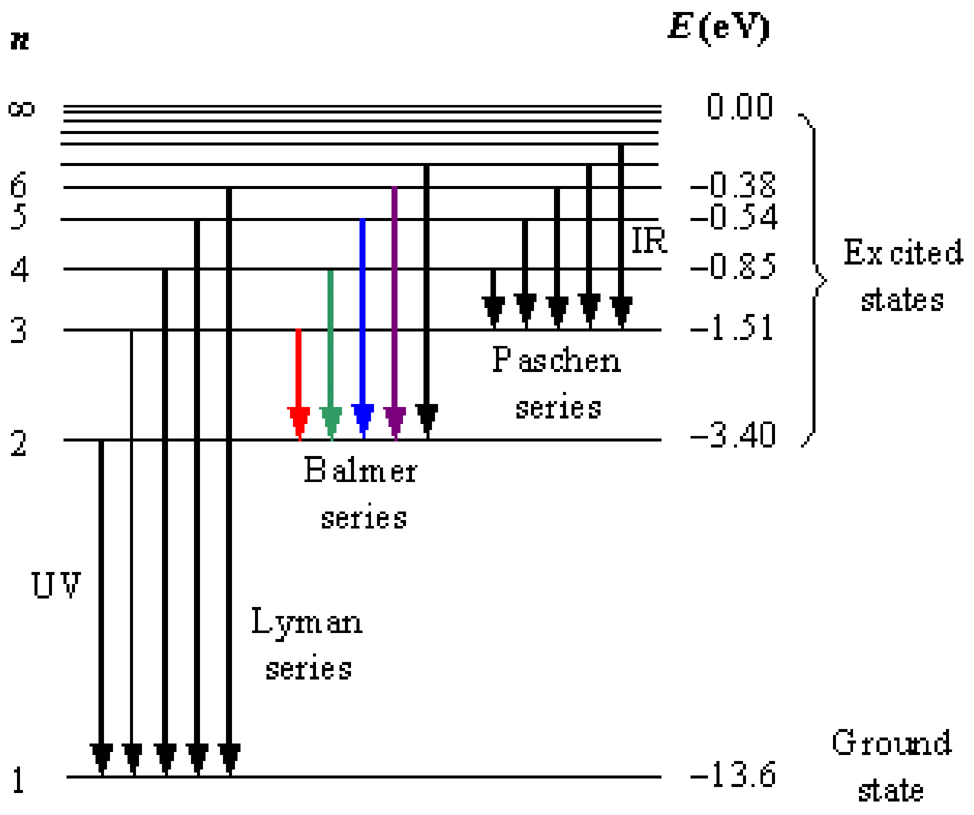
$$\therefore \text{ Total energy of electron } = -\frac{e^2}{8\pi\varepsilon_0 r}$$

$$\text{But } r = \frac{\varepsilon_0 n^2 h^2}{\pi m e^2}$$

$$\therefore \text{ Total energy of electron } = -\frac{e^2}{8\pi\varepsilon_0} \cdot \frac{\pi m e^2}{\varepsilon_0 n^2 h^2}$$

$$\therefore \text{ Total energy of electron } = -\frac{m e^4}{8\varepsilon_0^2 n^2 h^2}$$

Spectral Series of H atom



Energy levels of the hydrogen atom with some of the transitions between them that give rise to the spectral lines indicated.