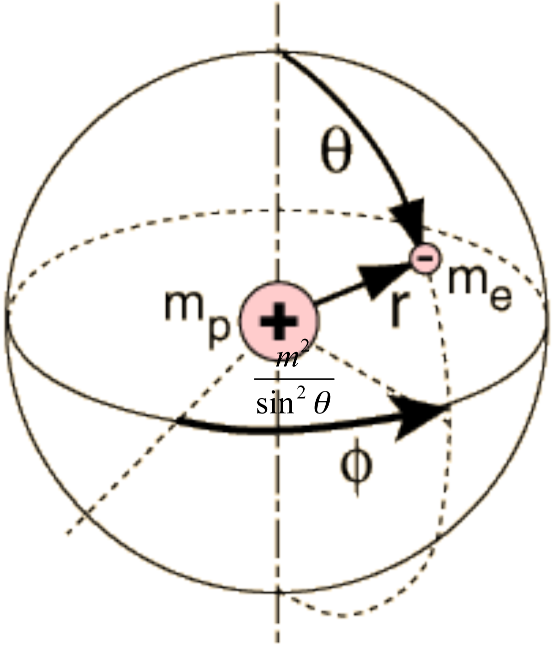
The Hydrogen Atom



A Completely Solvable problem!!

(kind of rare, in QM!)

General Approach to Solve H-atom problem

Formulate a correct Hamiltonian (energy) Operator H

Solve HΨ=EΨ (2nd order PDE) by separation of variable and intelligent trial/guess solutions

Impose boundary conditions for eigenfunctions (restriction) and obtain Quantum Numbers

Eigenstates or Wavefunctions: Should be "well behaved" - Normalization of Wavefunction

Energies of states Corresponding to Quantum Numbers

Probability and Average Values

Quantum Numbers that specify the "state" of the system

H-Atom: Constructing H=T+V

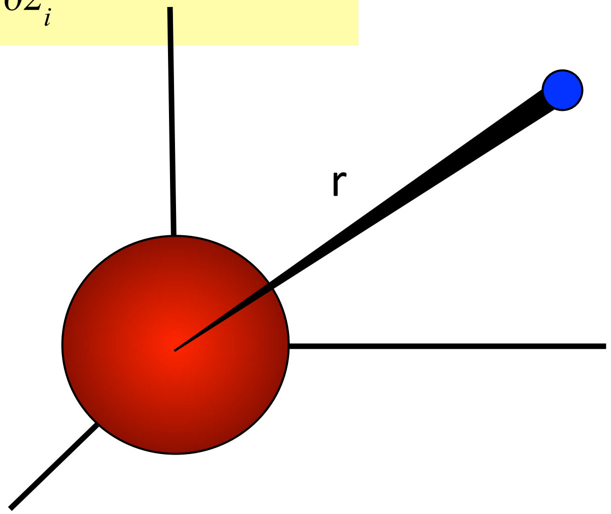
$$\widehat{H} = KE + PE = \frac{\widehat{P}^2(x,y,z)}{2m} + \widehat{V}(x,y,z) = -\sum_{i=1}^{N}\frac{\hbar^2}{2m_i}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right) + V(x,y,z)$$

$$\because\ \widehat{P} = -i\hbar\left(\frac{\partial}{\partial x}+\frac{\partial}{\partial y}+\frac{\partial}{\partial z}\right)\ and\ V(x,y,z) = Potential\ energy$$

$$\widehat{H} = -\sum_{i=1}^{N}\frac{\hbar^2}{2m_i}\nabla_i^2 + \widehat{V},\ where\ \nabla_i^2(Laplacian) = \frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2};\ i \rightarrow particles$$

Hydrogenic Atoms: 2-Particle System

1 electron moving around a
(massive) central nucleus (+ve)



$$\widehat{H} = -\frac{\hbar^2}{2m_{Nucleus}}\nabla^2_{Nucleus} - \frac{\hbar^2}{2m_{Electron}}\nabla^2_{Electron} + \widehat{V}_{Electron-Nucleus}$$

Potential Energy: Coulomb Potential

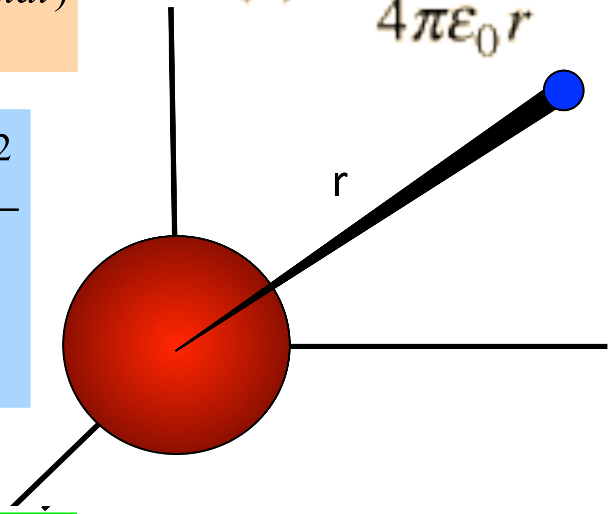
$$\widehat{H} = -\frac{\hbar^2}{2m_{Nucleus}}\nabla^2_{Nucleus} - \frac{\hbar^2}{2m_{Electron}}\nabla^2_{Electron} + \widehat{V}_{Electron-Nucleus}$$

$$Potential\ Energy:\ \hat{V} = U(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \sim -\frac{Ze^2}{r}\quad (Coulomb\ Potential)$$

$$U(r) = \frac{-e^2}{4\pi\varepsilon_0 r}$$

$$\widehat{H} = -\frac{\hbar^2}{2m_N}\left(\frac{\partial^2}{\partial x_N^2}+\frac{\partial^2}{\partial y_N^2}+\frac{\partial^2}{\partial z_N^2}\right) - \frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_e^2}+\frac{\partial^2}{\partial y_e^2}+\frac{\partial^2}{\partial z_e^2}\right) - \frac{Ze^2}{r}$$

$$where\ r = \sqrt{(x_e - x_N)^2 + (y_e - y_N)^2 + (z_e - z_N)^2}$$



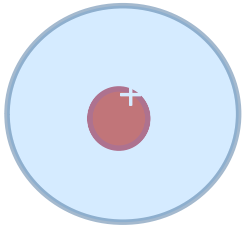
$$If\ \Psi_{Total} = Complete\ Wavefunction\ for\ H-Atom:\ TISE\ becomes$$

$$-\frac{\hbar^2}{2m_N}\nabla^2_N\Psi_{Total} - \frac{\hbar^2}{2m_e}\nabla^2_e\Psi_{Total} - \frac{Ze^2}{r}\Psi_{Total} = E_{Total}\Psi_{Total},$$

$$where\ \Psi_{Total} = \Psi(x_e, y_e, z_e, x_N, y_N, z_N)\ and\ E_{Total} = E_e + E_N$$

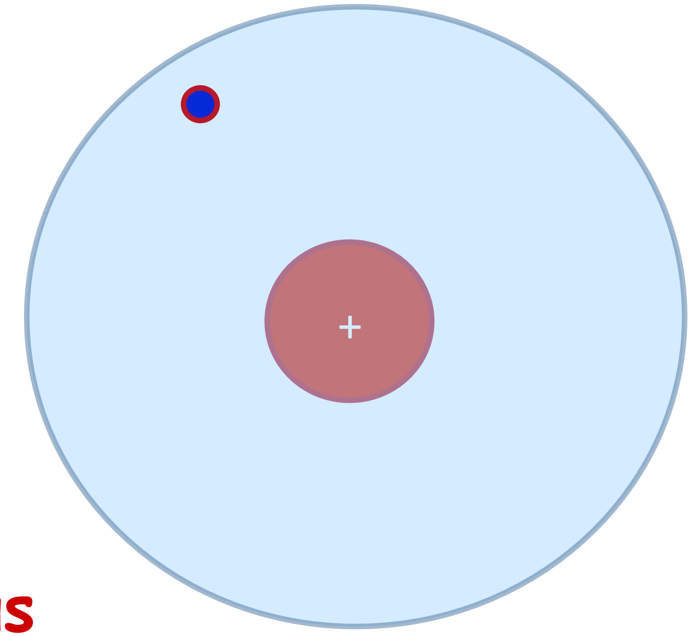
Schrodinger Eq. for Hydrogen Atom

$$-\frac{\hbar^2}{2m_N}\nabla_N^2\Psi\left(\vec{r_e},\vec{r_N}\right)-\frac{\hbar^2}{2m_e}\nabla_e^2\Psi\left(\vec{r_e},\vec{r_N}\right)-\frac{Ze^2}{r}\Psi\left(\vec{r_e},\vec{r_N}\right)=E_{Total}\Psi\left(\vec{r_e},\vec{r_N}\right)$$



Movement of the whole atom in absence of field

Separation of these two motions Can be done → Center of Mass And relative electronic coordinates



Relative motion of Electron with respect to Nucleus

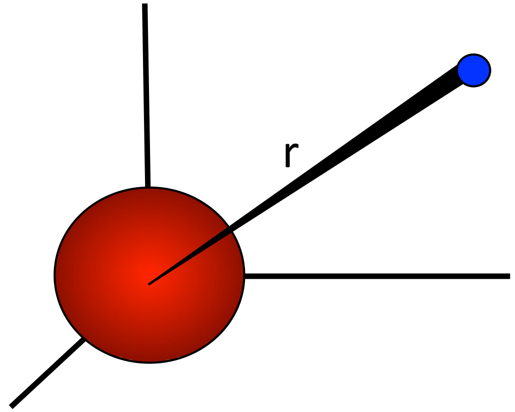
Reduced form of TISE for H-Atom: Transformation of coordinates

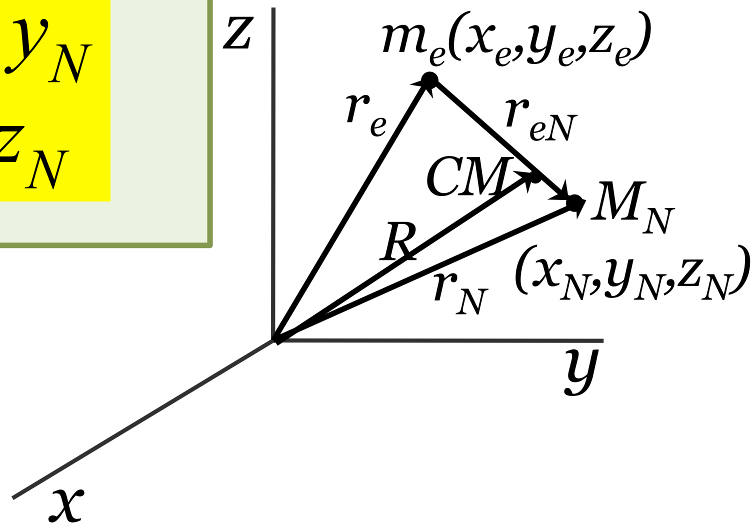
Two particle system: nucleus and electron with co-ordinates (x_N, y_N, z_N) & (x_e, y_e, z_e)

The potential energy depends on the relative co-ordinate, r_{eN}

$$\vec{r} = \overrightarrow{r_{eN}} = ix + jy + kz$$

$$x = x_e - x_N$$
$$y = y_e - y_N$$
$$z = z_e - z_N$$





Center of Mass (CM) Coordinates:

$$\vec{R} = iX + jY + kZ \qquad \vec{R} = \frac{m_e \vec{r_e} + m_N \vec{r_N}}{m_e + m_N}$$

$$X = \frac{m_e x_e + m_N x_n}{m_e + m_N}, Y = \frac{m_e y_e + m_N y_n}{m_e + m_N}, Z = \frac{m_e z_e + m_N z_n}{m_e + m_N}$$

Separation to Relative Frame

$$\left(-\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{QZe^2}{r_{eN}} \right)\Psi_{Total} = E_{Total}\cdot\Psi_{Total}$$

$$\Downarrow$$

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{QZe^2}{r} \right)\Psi_{Total} = E_{Total}\cdot\Psi_{Total}$$

where $M = m_e + m_N$ and $\mu = \dfrac{m_e m_N}{m_e + m_N}$

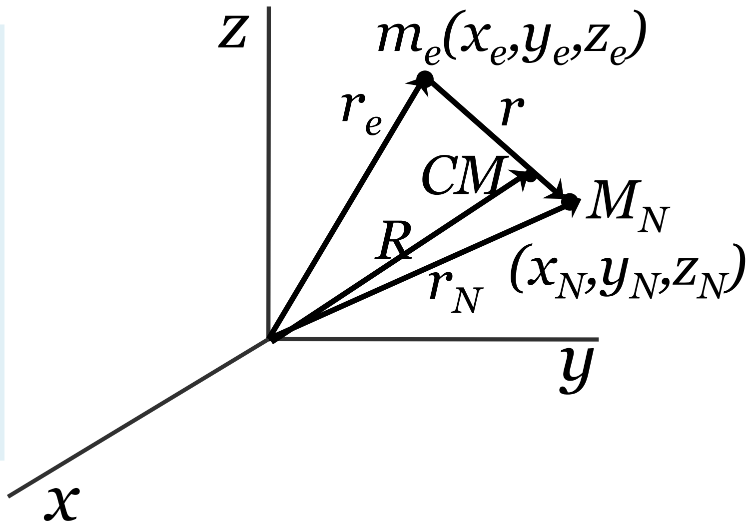
Separation to Relative Frame

$$\vec{r} = i x + j y + k z$$

$$\vec{R} = i X + j Y + k Z$$

$$\vec{r} = \vec{r}_{eN} = \vec{r}_e - \vec{r}_N$$

$$\vec{R} = \frac{m_e \vec{r}_e + m_N \vec{r}_N}{m_e + m_N}$$



$$\hat{H} = -\frac{\hbar^2}{2m_N}\left(\frac{\partial^2}{\partial x_N^2} + \frac{\partial^2}{\partial y_N^2} + \frac{\partial^2}{\partial z_N^2}\right) - \frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 \left|\vec{r}_e - \vec{r}_N\right|}$$

Let us look the KE operator in only 1 dimension, say x..

$$\hat{H}_{1D} = -\frac{\hbar^2}{2m_N}\left(\frac{\partial^2}{\partial x_N^2}\right) - \frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_e^2}\right)$$

$$X = \frac{m_e x_e + m_N x_n}{m_e + m_N}$$

$$x = x_e - x_N$$

Can we rewrite this KE operator in terms of X and x?

Separation to Relative Frame (in 1D)

$$\widehat{H}_{1D} = -\frac{\hbar^2}{2m_N}\left(\frac{\partial^2}{\partial x_N^2}\right) - \frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_e^2}\right)$$

$$X = \frac{m_e x_e + m_N x_n}{m_e + m_N} \qquad x = x_e - x_N$$

$$\frac{\partial}{\partial x_N} = \left(\frac{\partial X}{\partial x_N}\right)_{x_e}\frac{\partial}{\partial X} + \left(\frac{\partial x}{\partial x_N}\right)_{x_e}\frac{\partial}{\partial x}$$

$$\Downarrow$$

$$\frac{\partial}{\partial x_N} = \left(\frac{m_N}{m_N + m_e}\right)\frac{\partial}{\partial X} - \frac{\partial}{\partial x}$$

$$\frac{\partial}{\partial x_e} = \left(\frac{\partial X}{\partial x_e}\right)_{x_N}\frac{\partial}{\partial X} + \left(\frac{\partial x}{\partial x_e}\right)_{x_N}\frac{\partial}{\partial x}$$

$$\Downarrow$$

$$\frac{\partial}{\partial x_e} = \left(\frac{m_e}{m_N + m_e}\right)\frac{\partial}{\partial X} + \frac{\partial}{\partial x}$$

$$\widehat{H}_{1D} = -\frac{\hbar^2}{2m_N}\left(\frac{\partial^2}{\partial x_N^2}\right) - \frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_e^2}\right) \longrightarrow -\frac{\hbar^2}{2m_N}\left(\left(\frac{m_N}{m_N + m_e}\right)\frac{\partial}{\partial X} - \frac{\partial}{\partial x}\right)^2 - \frac{\hbar^2}{2m_e}\left(\left(\frac{m_e}{m_N + m_e}\right)\frac{\partial}{\partial X} + \frac{\partial}{\partial x}\right)^2$$

Separation to Relative Frame (in 1D)

$$-\frac{\hbar^2}{2m_N}\left(\frac{\partial^2}{\partial x_N^2}\right)-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_e^2}\right) \rightarrow -\frac{\hbar^2}{2m_N}\left(\left(\frac{m_N}{m_N+m_e}\right)\frac{\partial}{\partial X}-\frac{\partial}{\partial x}\right)^2-\frac{\hbar^2}{2m_e}\left(\left(\frac{m_e}{m_N+m_e}\right)\frac{\partial}{\partial X}+\frac{\partial}{\partial x}\right)^2$$

The cross term will cancel each other

$$-\frac{\hbar^2}{2m_N}\left(\frac{m_N^2}{(m_N+m_e)^2}\right)\frac{\partial^2}{\partial X^2}-\frac{\hbar^2}{2m_N}\frac{\partial^2}{\partial x^2}-\frac{\hbar^2}{2m_e}\left(\frac{m_e^2}{(m_N+m_e)^2}\right)\frac{\partial^2}{\partial X^2}-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2}$$

$$-\frac{\hbar^2}{2(m_N+m_e)}\frac{\partial^2}{\partial X^2}-\frac{\hbar^2}{2}\left(\frac{1}{m_N}+\frac{1}{m_e}\right)\frac{\partial^2}{\partial x^2}$$

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2}-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}$$

Where

$$M=m_N+m_e$$

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

H-Atom: Separation to Relative Frame

$$\left(-\frac{\hbar^2}{2m_N}\nabla_N^2-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{e^2}{r_{eN}}\right)\Psi_{Total}=E_{Total}\cdot\Psi_{Total}$$

$$\Psi_{Total}\left(x_e,y_e,z_e,x_N,y_N,z_N\right)\sim\Psi_{Total}\left(\vec{r},\vec{R}\right)$$

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2\boxed{-\frac{\hbar^2}{2\mu}\nabla_r^2-\frac{e^2}{r}}\right)\Psi_{Total}\left(\vec{r},\vec{R}\right)=E_{Total}\cdot\Psi_{Total}\left(\vec{r},\vec{R}\right)$$

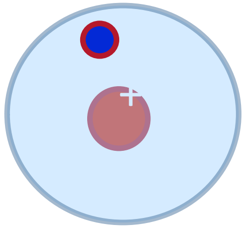
$$\Psi_{Total}\left(\vec{r},\vec{R}\right)=\Psi_e\left(\vec{r}\right)\bullet\Psi_{CM}\left(\vec{R}\right)$$

$$-\frac{\hbar^2}{2M}\nabla_{CM}^2\left(\vec{R}\right)\Psi_{CM}\left(\vec{R}\right)=E_{CM}\Psi_{CM}\left(\vec{R}\right)$$

Free Particle: movement of the whole atom!

$$\left(-\frac{\hbar^2}{2\mu}\nabla_e^2\left(\vec{r}\right)-\frac{Ze^2}{|r|}\right)\Psi_e\left(\vec{r}\right)=E_r\Psi_e\left(\vec{r}\right)$$

Relative motion of Electron with respect to Nucleus



Free Particle
movement of
the whole atom
We solved it!

$$-\frac{\hbar^2}{2M}\nabla^2_{CM}\Psi_{CM} = E_{CM}\Psi_{CM}$$

Relative
motion
of electron
wrt nucleus

$$\left(-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{|r|}\right)\Psi_r = E_r\Psi_r$$

We are only interested in
this part

H-Atom: Are we ready to solve TISE?

$$\left(-\frac{\hbar^2}{2\mu}\nabla_e^2\left(\vec{r}\right)-\frac{Ze^2}{|r|}\right)\Psi_e\left(\vec{r}\right)=E_r\Psi_e\left(\vec{r}\right)$$

$$\Psi_e\left(\vec{r}\right)\Rightarrow\Psi_e\left(x,y,z\right)\Leftrightarrow\Psi\left(x,y,z\right):\quad \text{3 variables}$$

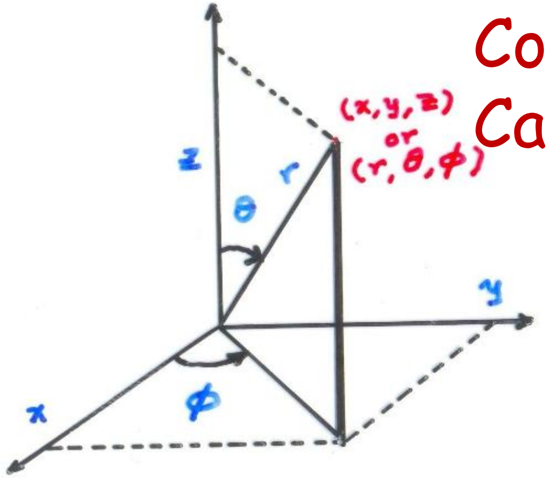
$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}\Psi\left(x,y,z\right)+\frac{\partial^2}{\partial y^2}\Psi\left(x,y,z\right)+\frac{\partial^2}{\partial z^2}\Psi\left(x,y,z\right)\right)$$

$$-\frac{Ze^2}{\sqrt{x^2+y^2+z^2}}\Psi\left(x,y,z\right)=E.\Psi\left(x,y,z\right)$$

Road-Block: This 2nd order PDE with ***3 variables…***

Can not be separated!!!

Spherical Polar Coordinates



Conversion from Cartesian coordinates

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

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

$$z = r \cos\theta$$

$$dV = r^2 \sin\theta \, dr \, d\theta \, d\phi$$

- 'r' ranges from 0 to ∞
- the co-latitude θ ranges from 0 (north pole) to π (south pole)
- the azimuth φ ranges from 0 to 2π

Used for spherically symmetric systems

Laplacian in Spherical Polar Co-ords.

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}\Psi(x,y,z)+\frac{\partial^2}{\partial y^2}\Psi(x,y,z)+\frac{\partial^2}{\partial z^2}\Psi(x,y,z)\right)$$

$$-\frac{Ze^2}{\sqrt{x^2+y^2+z^2}}\Psi(x,y,z)=E.\Psi(x,y,z)$$

$$x=r\sin\theta\cos\varphi,\quad y=r\sin\theta\sin\varphi,\quad z=r\cos\theta,$$

follows by the chain rule for partial differentiation that

$$\frac{\partial}{\partial x}=\frac{\partial r}{\partial x}\frac{\partial}{\partial r}+\frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta}+\frac{\partial\varphi}{\partial x}\frac{\partial}{\partial\varphi}=\boxed{\sin\theta\cos\varphi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta}-\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}}$$

$$\frac{\partial}{\partial y}=\frac{\partial r}{\partial y}\frac{\partial}{\partial r}+\frac{\partial\theta}{\partial y}\frac{\partial}{\partial\theta}+\frac{\partial\varphi}{\partial y}\frac{\partial}{\partial\varphi}=\boxed{\sin\theta\sin\varphi\frac{\partial}{\partial r}+\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}+\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}},$$

$$\frac{\partial}{\partial z}=\frac{\partial r}{\partial z}\frac{\partial}{\partial r}+\frac{\partial\theta}{\partial z}\frac{\partial}{\partial\theta}+\frac{\partial\varphi}{\partial z}\frac{\partial}{\partial\varphi}=\boxed{\cos\theta\frac{\partial}{\partial r}-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta}.}$$

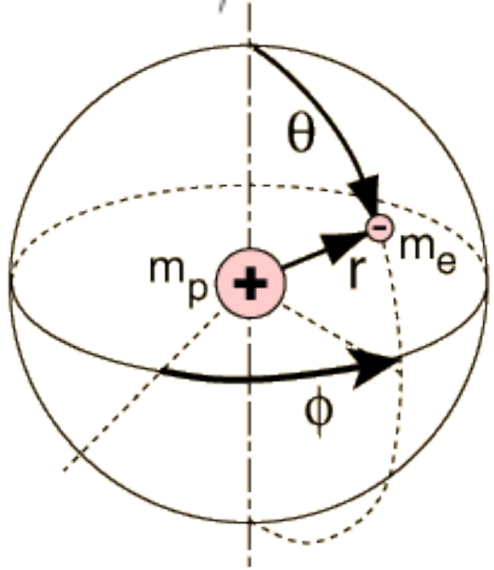
$$\boxed{\nabla^2_{r\theta\phi}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}}$$

Hamiltonian: Spherical Polar Coordinates

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

$$\hat{H}(r,\theta,\phi) = -\frac{\hbar^2}{2\mu}\nabla^2_{r\theta\phi} + V(r,\theta,\phi)$$

$$\hat{H}(r,\theta,\phi)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$



Schrödinger eq. in spherical polar coordinates

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi(r,\theta,\phi)$$

Looks can be deceiving!

$$-\frac{Ze^2}{r}\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

Solve this PDE →need to separate variables **r**, θ, φ: **POSSIBLE**

TISE for H-Atom in spherical-polar coordinates

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

$$+\frac{2\mu}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)\Psi(r,\theta,\phi) \quad = \quad 0$$

2nd order Partial Differential Equation with three variables

$$\textit{Special solution if } \widehat{H}=\widehat{H}(r)+\widehat{H}(\theta)+\widehat{H}(\phi): \quad \Psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$$

$$\frac{1}{r^2}\left[\begin{array}{l}\frac{d}{dr}\left(r^2\frac{d}{dr}\boxed{R(r)\left[\Theta(\theta).\Phi(\phi)\right]}\right)+\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\boxed{\Theta(\theta)\left[R(r).\Phi(\phi)\right]}\right)\\ \qquad +\frac{1}{\sin^2\theta}\frac{d^2}{d\phi^2}\boxed{\Phi(\phi)\left[R(r).\Theta(\theta)\right]}\end{array}\right]$$

$$+\frac{2\mu}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)\boxed{R(r)\Theta(\theta)\Phi(\phi)} \quad = \quad 0$$

Separation of Variables r, θ, ϕ

$$\Psi(r,\theta,\phi) = R(r).\Theta(\theta).\Phi(\phi) = R.\Theta.\Phi$$

$$\frac{1}{r^2}\left[\boxed{\Theta\Phi}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\boxed{R\Phi}}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{\boxed{R\Theta}}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2}\right]+\frac{2\mu}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)\boxed{R\Theta\Phi}=0$$

$$\textit{Multiply by } \frac{r^2\sin^2\theta}{R.\Theta.\Phi} \textit{ and rearrange}:$$

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2\mu}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)r^2\sin^2\theta=\boxed{-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}$$

$$LHS = F(r,\theta) = G(\phi) = RHS \Rightarrow F(r,\theta) = G(\phi) = Const. = m^2 (say)$$

$$\therefore \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+m^2=0$$

Solve 2nd order DE to obtain functional form of Φ(ϕ)

Solving ϕ-part is relatively simple!

$$\therefore \frac{1}{\Phi(\phi)}\frac{d^2}{d\phi^2}\Phi(\phi)+m^2=0$$

$$Solution: \quad \Phi(\phi)=Ae^{\pm im\phi}$$

$$\because \frac{d\Phi}{d\phi}=\pm im\Phi$$

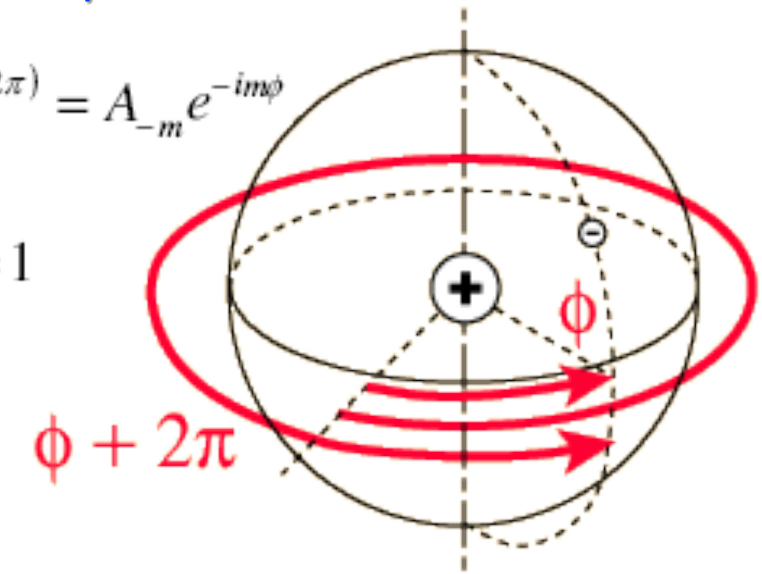
$$\& \ \frac{d^2\Phi}{d\phi^2}=-m^2\Phi$$

$$\Phi(\phi+2\pi)=\Phi(\phi)$$

Boundary Condition

$$\Rightarrow \quad A_m e^{im(\phi+2\pi)}=A_m e^{im\phi} \quad \text{and} \quad A_{-m}e^{-im(\phi+2\pi)}=A_{-m}e^{-im\phi}$$

$$\therefore \quad e^{im(2\pi)}=1 \quad \text{and} \quad e^{-im(2\pi)}=1$$



This is only true if $\boxed{m=0,\ \pm1,\ \pm2,\ \pm3,....}$

m is the "magnetic" quantum number

Another Quantum Number "popped out" out of Boundary Conditions: Quantization of Angular Momentum!

Magnetic Quatnum Number: Can take any integral value (including zero); Restricted by another quantum number (m<l). Loosely relates to direction of orbital angular momentum; splitting of energy levels in magnetic field.

Solving R(r) and $\Theta(\theta)$ part not so simple, but can be done (in ~5-6 lectures!)

$$\frac{\boxed{\sin^2\theta}}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\boxed{\sin\theta}}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)\boxed{\sin^2\theta}-m^2=0$$

Simply divide by $\sin^2\theta$ *and rearrange:*

$$\underbrace{\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)}}_{\text{Only r : Can be solved to obtain R(r) part}}=\underbrace{\boxed{\frac{m^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)}}_{\text{Only }\theta\text{: Can be solved to obtain }\Theta(\theta)\text{ part}}=\beta(const.)$$

Only r : Can be solved to obtain R(r) part

Only θ: Can be solved to obtain $\Theta(\theta)$ part

Boundary conditions applied!

Need mathematical skills to solve the Differential Equations for R(r) and $\Theta(\theta)$ - it will take several lectures to do so….

Solve for R(r): Quantized Energies

Radial Wavefunction depends on n and l:

$$R_{nl}(r) = -\left[\frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2}\left(\frac{2Z}{na_0}\right)^{l+3/2} r^l e^{-Zr/na_0} L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

n= Principal Quantum Number=1,2,3,…

where $L_{n+l}^{2l+1}(2Zr/na_0)$ are the *associated Laguerre functions*,

Energies: E_n:

$$E = \frac{-Z^2e^2}{8\pi\varepsilon_0 a_0 n^2} = \frac{-Z^2\mu e^4}{8\varepsilon_0^2 h^2 n^2} \quad n = 1,2,3,\ldots$$

Essentially same as Bohr's Equation, with slight changes

$E = -Z^2e^2/8\pi\varepsilon_0 a_0$ lowest energy eigenvalue

$a_0 \equiv \varepsilon_0 h^2/\pi\mu e^2$ Bohr radius

$$E = -\frac{Z^2me^4}{8n^2h^2\varepsilon_0^2} = \frac{-13.6Z^2}{n^2}eV$$

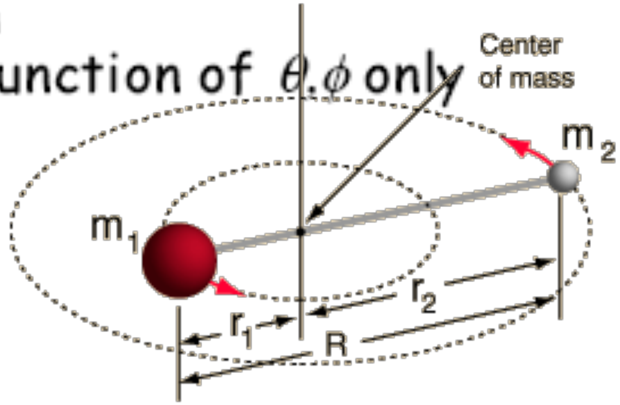
Energy of H-atom in absence of external fields depend Only on principal quantum number; Total energy accounts for kinetic energy and potential energy of the electron in presence of a positively charged nucleus

$\Theta(\theta)\Phi(\phi)$ are Spherical Harmonics $Y^l_m(\theta,\phi)$

Easier to solve if written differently: Rigid-Rotor → already solved the angular (θ, ϕ) part: Related to Angular Momentum!

$$\underbrace{\left[-\hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + 2\mu r^2 \left[U(r) - E\right]\right]}_{\text{function of } r \text{ only}} \psi(r,\theta,\phi) + \hat{L}^2 \psi(r,\theta,\phi) = 0$$

function of θ, ϕ only



$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi(\theta,\phi) = \widehat{L}^2\Psi(\theta,\phi)$$

L^2 → Square of angular momentum:
Eigenfunctions "Spherical Harmonics"

Angular momentum: solutions are spherical harmonic wavefunctions Y_l^m

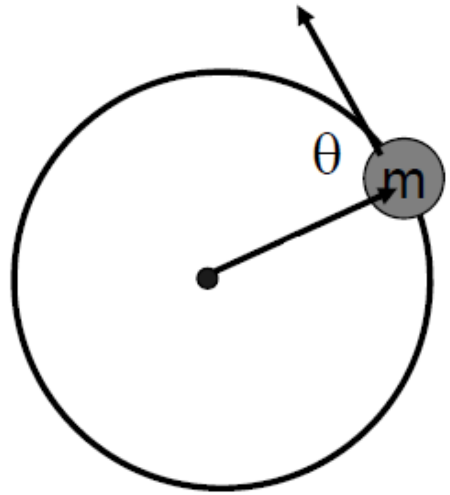
$$\psi(r,\theta,\phi) = R(r) Y_l^m(\theta,\phi)$$

l=Azimuthal Quantum Number
or orbital quantum number l≤n-1

with $\hat{L}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi) \quad l = 0,1,2,\ldots$

Rotational Motion in Classical Physics

Angular Momentum (L)



$$L = \vec{r} x \vec{p}$$

Magnitude: $L = rp\sin(\theta)$

Circular Motion: $L = rp\sin(90^0) = rp$

or: $L = rp = rmv = \left(mr^2\right)\left(\frac{v}{r}\right) = (mr^2)\omega$

$L = I\omega$ where $I = mr^2$ $\omega = \frac{v}{r}$

Moment of Inertia **Angular Frequency**

Energy

$$E = \frac{p^2}{2m} = \frac{mv^2}{2} = \frac{m(r\omega)^2}{2} = \frac{mr^2\omega^2}{2} = \frac{I\omega^2}{2}$$ or: $$E = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$$

Angular Momentum in Quantum Mechanics

Classical Angular Momentum

$$\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$$

$$\vec{p} = p_x\vec{i} + p_y\vec{j} + p_z\vec{k}$$

$$\vec{L} = \vec{r}x\vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$L_x = yp_z - zp_y$$
$$L_y = zp_x - xp_z$$
$$L_z = xp_y - yp_x$$

$$\vec{L} = (yp_z - zp_y)\vec{i} + (zp_x - xp_z)\vec{j} + (xp_y - yp_x)\vec{k}$$

Angular Momentum in Quantum Mechanics

QM Angular Momentum Operators

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

It may be shown that

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial \varphi} = \frac{\hbar}{i}\frac{\partial}{\partial \varphi}$$

$$\hat{L}^2 = \hat{L}_x \bullet \hat{L}_x + \hat{L}_y \bullet \hat{L}_y + \hat{L}_z \bullet \hat{L}_z$$

It may be shown that

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

$$L^2 = \hat{L}_x \bullet \hat{L}_x + \hat{L}_y \bullet \hat{L}_y + \hat{L}_z \bullet \hat{L}_z$$

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi(\theta,\phi) = \widehat{L^2}\Psi(\theta,\phi)$$

Particle in 3D-Box: Three Quantum Numbers

$$\psi_{n_x n_y n_z}(x,y,z) = \left(\frac{8}{abc}\right)^{\frac{1}{2}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad n_x = 1,2,3,\ldots \quad n_y = 1,2,3,\ldots \quad n_z = 1,2,3,\ldots$$

3 Quantum Numbers needed to Describe the system completely

Normalization Conditions (each dimension)

The 3D product states are naturally normalized if the 1D wavefunctions are normalized:

$$\iiint \psi_x^*(x)\psi_y^*(y)\psi_z^*(z)\psi_x(x)\psi_y(y)\psi_z(z)\,dx\,dy\,dz =$$

$$\underbrace{\int \psi_x^*(x)\psi_x(x)\,dx}_{1} \times \underbrace{\int \psi_y^*(y)\psi_y(y)\,dy}_{1} \times \underbrace{\int \psi_z^*(z)\psi_z(z)\,dz}_{1} = 1$$

H-Atom: Three Quantum Numbers

$$\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)}=\beta(const.)$$

n = principle quantum no

$$\boxed{\frac{m^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)}=\beta(const.)$$

l = Azimuthal quantum no

$$\therefore \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+m^2=0$$

m_l = magnetic quantum no

Interestingly, there are restrictions on the values of the individual quantum no's