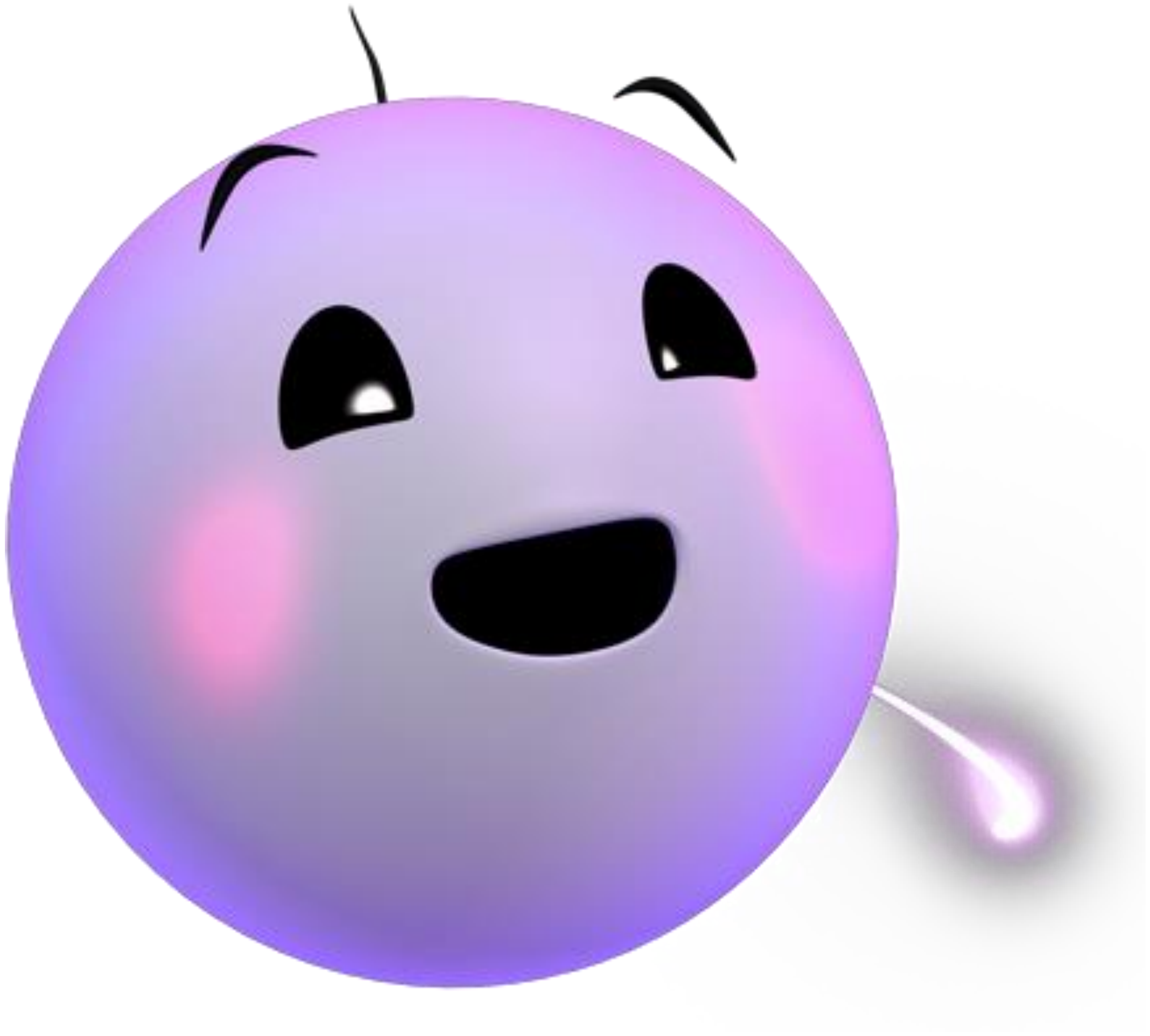
Hydrogen Atom: Schrodinger equation



http://www.moleculestothemax.com/

Recapitulation: Basics of Quantum Mechanics

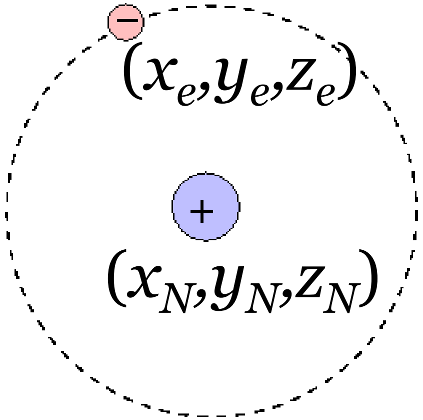
- Schrödinger equation: Classical wave equation for de Broglie waves

- Eigenvalue equation: $\hat{A}\psi = a\psi$

- Expectation values: $$\frac{\int \psi^* \hat{A}\psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

- Boundary conditions: Quantization

Hydrogen Atom



Two particle central-force problem

Completely solvable – a rare example!

Hydrogen Atom

$$\widehat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon_o}\frac{Z_N Z_e e^2}{r_{eN}}$$

Schrodinger Equation

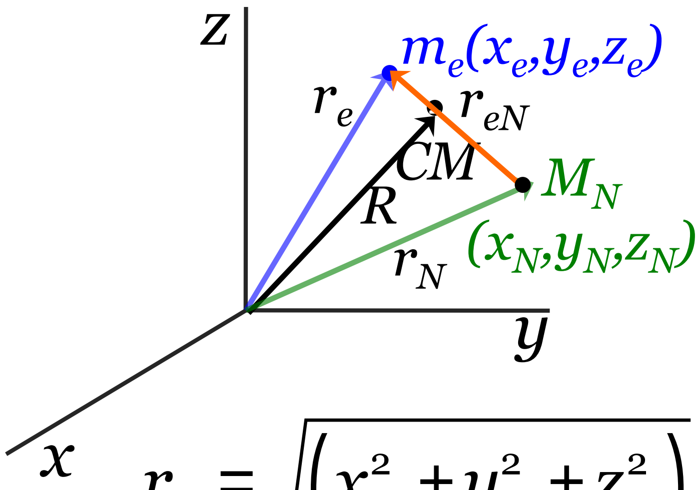
$$\left[-\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{QZe^2}{r_{eN}}\right]\Psi_{Total} = E_{Total}\cdot\Psi_{Total}$$

$$Y_{Total} = Y(x_N, y_N, z_N, x_e, y_e, z_e)$$

Hydrogen Atom: Relative Frame of Reference

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

Separation of $\hat{H}$ into Center of Mass and Internal co-ordinates



$$r_N=\sqrt{\left(x_N^2+y_N^2+z_N^2\right)}$$

$$r_e=\sqrt{\left(x_e^2+y_e^2+z_e^2\right)}$$

$$x=x_e-x_N$$

$$y=y_e-y_N$$

$$z=z_e-z_N$$

$$r=r_{eN}=r_e-r_N$$
$$=\sqrt{\left(x^2+y^2+z^2\right)}$$

$$X=\frac{m_ex_e+m_Nx_n}{m_e+m_N}$$

$$Y=\frac{m_ey_e+m_Ny_n}{m_e+m_N}$$

$$Z=\frac{m_ez_e+m_Nz_n}{m_e+m_N}$$

$$R=\frac{m_er_e+m_Nr_N}{m_e+m_N}$$

Hydrogen Atom: Relative Frame of Reference

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

$$\Downarrow$$

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

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

Checkout Appendix-1

Hydrogen Atom: Separation to Relative Frame

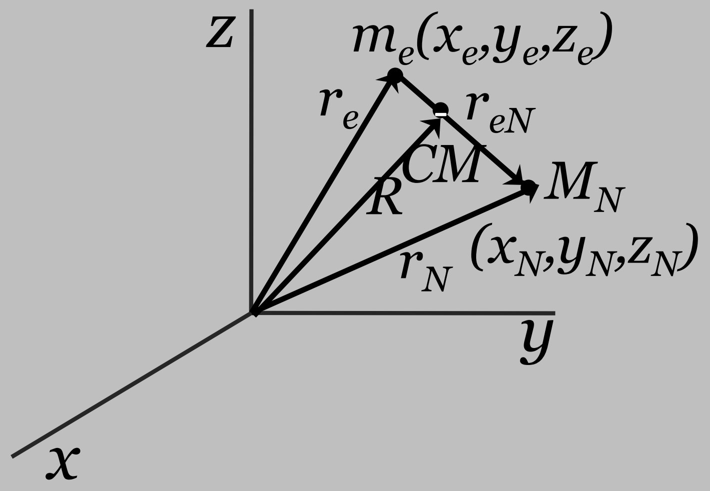
Appendix-1

Hydrogen atom has two particles the nucleus and electron with co-ordinates x_N, y_N, z_N and x_e, y_e, z_e

The potential energy between the two is function of relative co-ordinates $x = x_e - x_N$, $y = y_e - y_N$, $z = z_e - z_N$

$$r = ix + jy + kz$$

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



$$R = iX + jY + kZ$$

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

Hydrogen Atom: Separation to Relative Frame

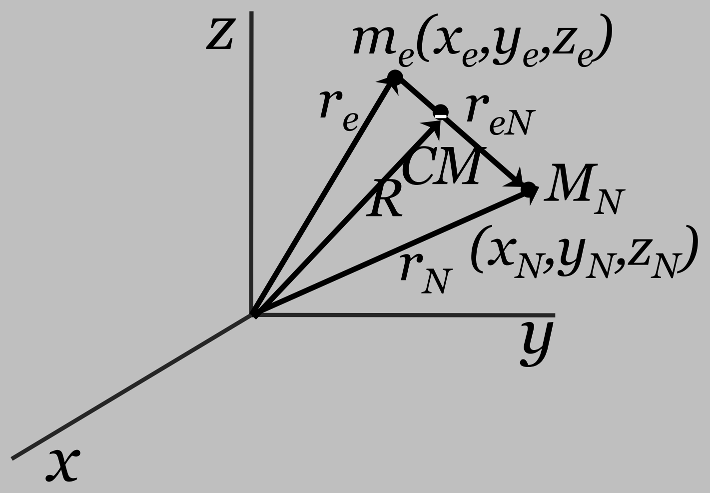
Appendix-1

$$R = \frac{m_e r_e + m_N r_N}{m_e + m_N}$$

$$r = r_{eN} = r_e - r_N$$

$$r_e = R - \frac{m_N}{m_e + m_N} r$$

$$r_N = R - \frac{m_e}{m_e + m_N} r$$



Hydrogen Atom: Separation to Relative Frame

Appendix-1

$$T = \frac{1}{2} m_e \left|\dot{r}_e\right|^2 + \frac{1}{2} m_N \left|\dot{r}_N\right|^2$$

$$T = \frac{1}{2} m_e \left(\dot{R} - \frac{m_N}{m_e + m_N} \dot{r} \right) \cdot \left(\dot{R} - \frac{m_N}{m_e + m_N} \dot{r} \right)$$

$$+ \frac{1}{2} m_e \left(\dot{R} - \frac{m_e}{m_e + m_N} \dot{r} \right) \cdot \left(\dot{R} - \frac{m_e}{m_e + m_N} \dot{r} \right)$$

$$T = \frac{1}{2} \left(m_e + m_N \right) \left|\dot{R}\right|^2 + \frac{1}{2} \left(\frac{m_e m_N}{m_e + m_N} \right) \left|\dot{r}\right|^2$$

$$T = \frac{1}{2} M \left|\dot{R}\right|^2 + \frac{1}{2} \mu \left|\dot{r}\right|^2 \quad \text{where } M = m_e + m_N \quad \text{and} \quad \mu = \frac{m_e m_N}{m_e + m_N}$$

$$\dot{r}_e = \frac{dr_e}{dt}$$

$$\dot{r}_N = \frac{dr_N}{dt}$$

$$\dot{r} = \frac{dr}{dt}$$

$$\dot{R} = \frac{dR}{dt}$$

Hydrogen Atom: Separation to Relative Frame

Appendix-1

$$T = \frac{1}{2}M\left|\dot{R}\right|^2 + \frac{1}{2}\mu\left|\dot{r}\right|^2$$

$$T = \frac{p_R^2}{2M} + \frac{p_r^2}{2\mu}$$

In the above equation the first term represent the kinetic energy of the center of mass (CM) motion and second term represents the kinetic energy of the relative motion of electron and

$$H = \frac{p_R^2}{2M} + \frac{p_r^2}{2\mu} - \frac{Z_N \cdot Z_e}{r}$$

$$\widehat{H} = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Z_N \cdot Z_e}{r}$$

Hydrogen Atom: Separation of CM motion

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

$$\widehat{H} = \widehat{H}_N + \widehat{H}_e \qquad \Psi_{Total} = \chi_N \times \psi_e \qquad E_{Total} = E_N + E_e$$

$$\widehat{H}_N\chi_N = \left(-\frac{\hbar^2}{2M}\nabla_R^2\right)\chi_N = E_N\chi_N$$

$$E_N = \; ?$$

Hydrogen Atom: Electronic Hamiltonian

$$\widehat{H}_e \cdot \psi_e = \left(-\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{QZe^2}{r} \right) \psi_e = E_e \cdot \psi_e$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

y_e Þ $y_e(x,y,z)$

Hydrogen Atom: Electronic Hamiltonian

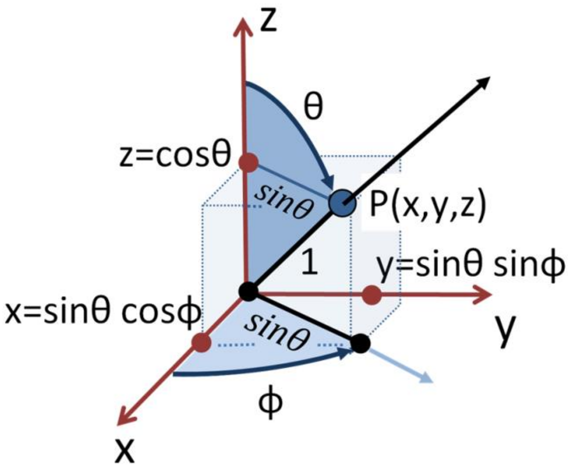
$$\hat{H}_e \cdot \psi_e = \left(-\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{QZe^2}{r} \right) \psi_e = E_e \cdot \psi_e$$

$$y_e \text{ Þ } y_e(x,y,z)$$

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_e(x,y,z) - \frac{QZe^2}{\sqrt{\left(x^2 + y^2 + z^2\right)}} \psi_e(x,y,z) = E_e \cdot \psi_e(x,y,z)$$

Not possible to separate out into three different co-ordinates.
Need a new co-ordinate system

Spherical Polar Co-ordinates

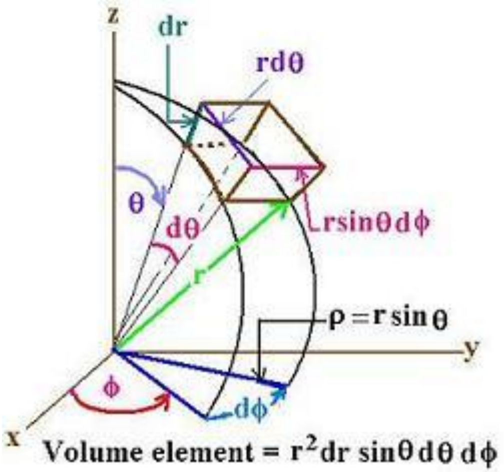


$$z = r\cos q$$
$$x = r\sin q\cos f$$
$$y = r\sin q\sin f$$

r: 0 to ∞

θ: 0 to π

ϕ: 0 to 2π



$$r = \sqrt{\left(x^2 + y^2 + z^2\right)}$$
$$\theta = \cos^{-1}\left(\frac{z}{r}\right)$$
$$\phi = \tan-1\left(\frac{y}{x}\right)$$

$$dt = r^2 \times dr \times \sin q \times dq \times df$$

Laplacian in Spherical Coordinates

Kinetic energy operator in Spherical Coordinates

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

Hamiltonian in Spherical Coordinates

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

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

Schrodinger equation for the electronic part in Spherical Polar Co-ordinates

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

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

Schrodinger equation for the electronic part in Spherical Polar Co-ordinates

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

$$-\frac{QZe^2}{r}\psi_e = E_e\psi_e$$

Multiply with $\frac{-2\mu r^2}{\hbar^2}$ and bring all the terms to the LHS

Separation of variables

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

$$+\frac{2\mu rQZe^2}{\hbar^2}\psi_e+\frac{2\mu r^2}{\hbar^2}E_e\psi_e=0$$

Separation of variables

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial(R\cdot\Theta\cdot\Phi)}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial(R\cdot\Theta\cdot\Phi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2(R\cdot\Theta\cdot\Phi)}{\partial\phi^2}$$

$$+\frac{2\mu rQZe^2}{\hbar^2}(R\cdot\Theta\cdot\Phi)+\frac{2\mu r^2}{\hbar^2}E_e(R\cdot\Theta\cdot\Phi)=0$$

Upon differentiation

Separation of variables

$$\boxed{(\Theta\cdot\Phi)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\boxed{(R\cdot\Phi)}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\boxed{(R\cdot\Theta)}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}$$

$$+\frac{2\mu rQZe^2}{\hbar^2}(R\cdot\Theta\cdot\Phi)+\frac{2\mu r^2}{\hbar^2}E_e(R\cdot\Theta\cdot\Phi)=0$$

Multiply with $\dfrac{1}{R\cdot\Theta\cdot\Phi}$

Separation of variables

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=0$$

Rearrange

Radial **Angular**

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=-\left[\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right]$$

$$=\beta$$

A constant

Separation of variables

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

Radial equation

$$\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}=-\beta$$

Angular equation

Separation of variables

Radial equation

Angular equation

$$\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}=-\beta$$

Multiply with $\sin^2\theta$ and rearrange

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

Separation of variables

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r Q Z e^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

The three variables r, θ and ϕ are separated

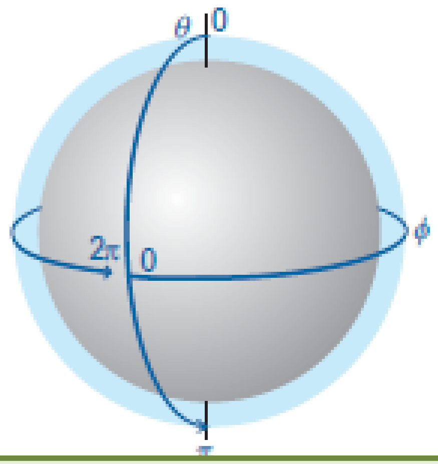
Solution to ϕ part

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

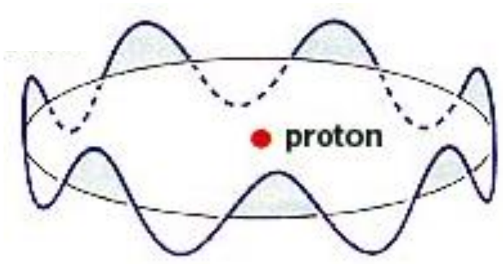
$$\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2\Phi(\phi)$$

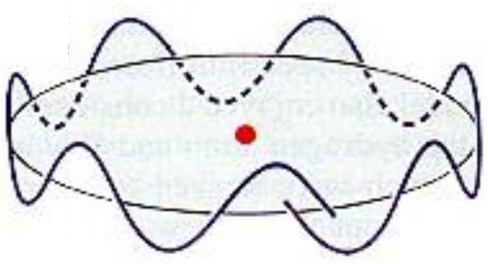
Trial solution: $\Phi(\phi)=Ae^{\pm im\phi}$

$$\frac{\partial\Phi}{\partial\phi}=\pm im\Phi$$



‘ϕ’ ranges from 0 to 2π





Wavefunction has to be single-valued $\Rightarrow \Phi(\phi+2\pi)=\Phi(\phi)$

Periodic Boundary Condition

Moment of truth

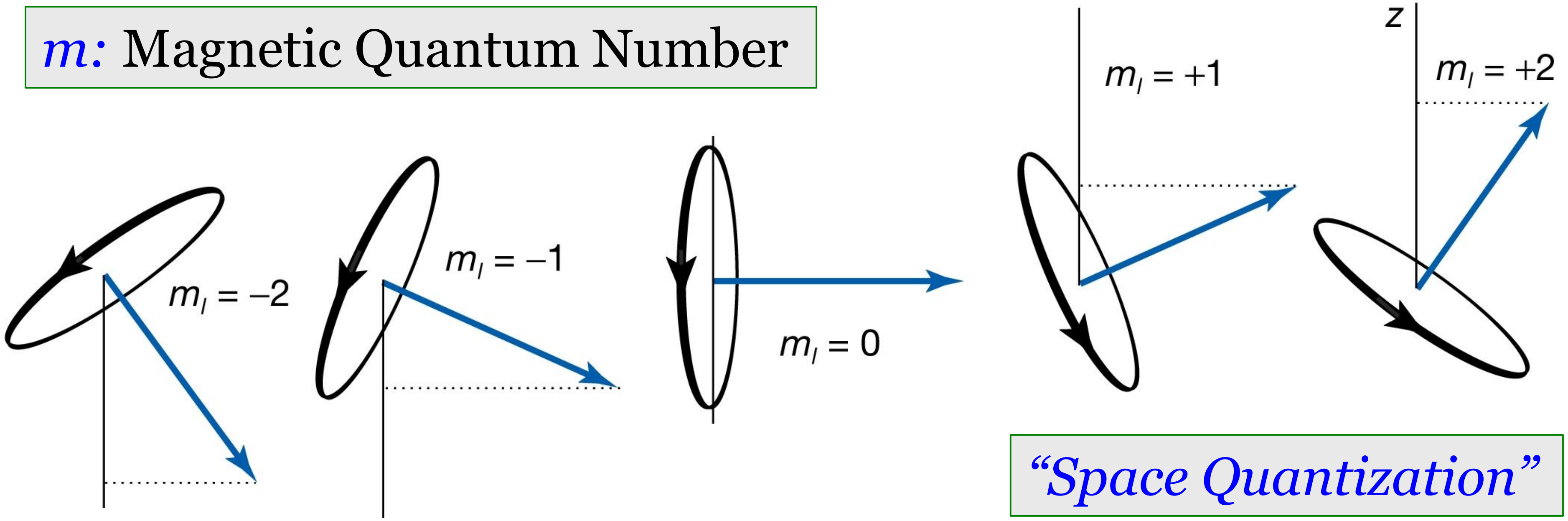
$$\widehat{L_z} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

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

$$\widehat{L_z}\Phi =$$

z-component of angular momentum

m: Magnetic Quantum Number



"Space Quantization"

Solution to ϕ part: Magnetic quantum number

- m=0, ±1, ±2, ±3, ±4,….
- m is the **magnetic quantum number**
- m is restricted by another quantum number (orbital Angular momentum), l, such that $|m|<l$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$