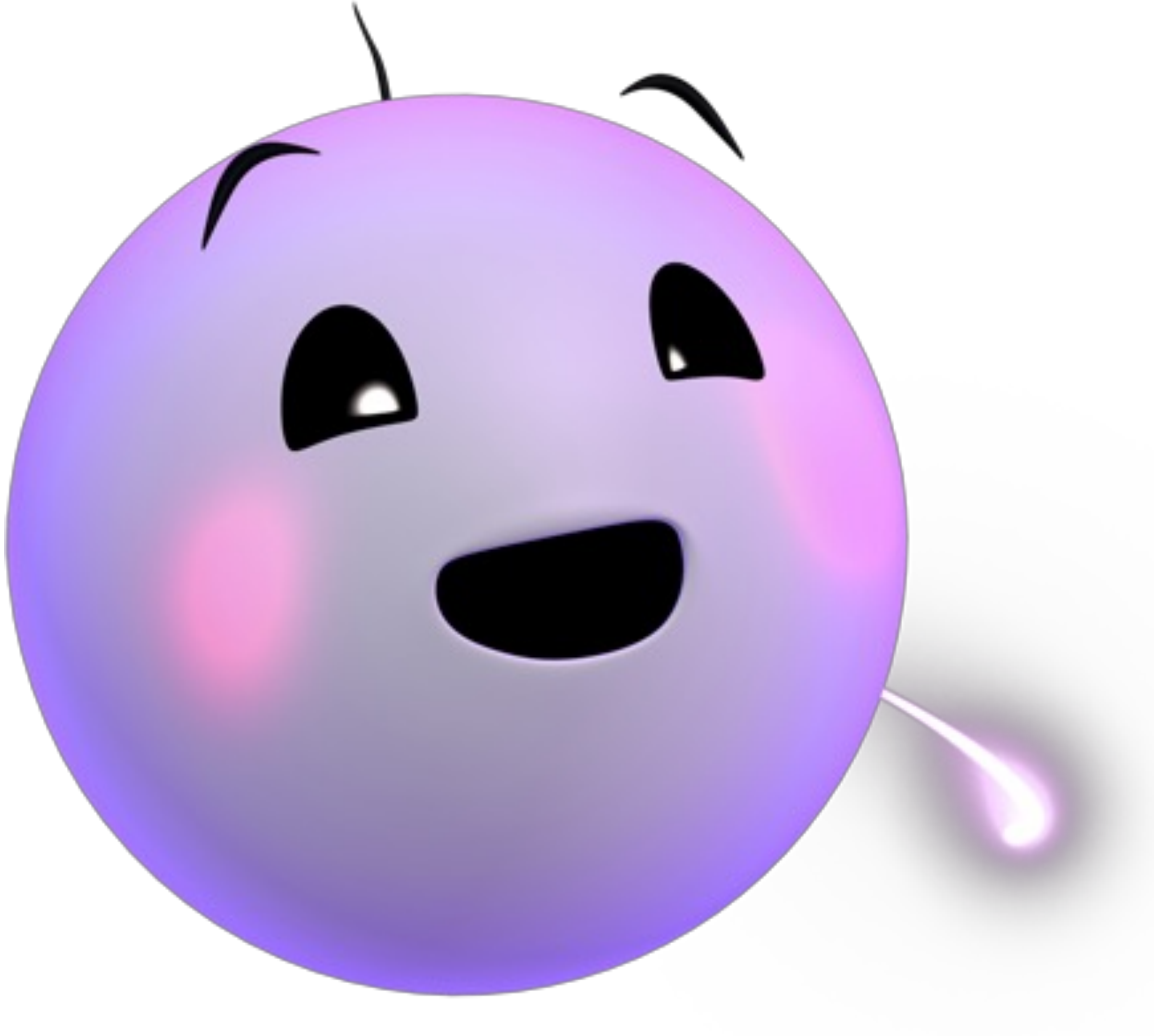
Lecture 4: Hydrogen Atom



http://www.moleculestothemax.com/

What have we learnt?

Formulate a correct Hamiltonian (energy) Operator H

↓

Solve TISE $H\Psi = E\ \Psi$ by separation of variables and intelligent trial wavefunction

↓

Impose boundary conditions for eigenfunctions and obtain Quantum numbers

↓

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

↓

Probabilities and Expectation Values

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

Recapitulation: Free Particle

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\cdot\psi(x)$$

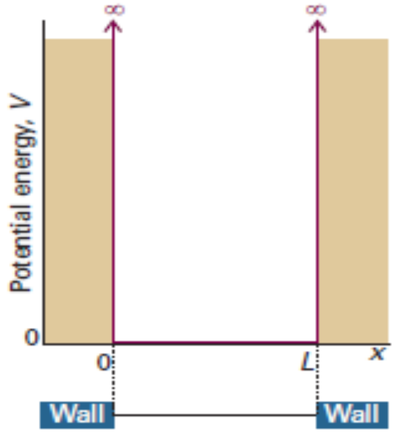
$$\boxed{\psi(x) = A\sin kx + B\cos kx}$$

$$\frac{\hbar^2}{2m}k^2\psi(x) = E\cdot\psi(x)$$

$$\boxed{\psi(x) = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x}$$

No Quantization, all energies are allowed

Recapitulation: Particle in 1-D Square-Well Potential



$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

$$\boxed{\psi(x) = A\sin kx + B\cos kx}$$

Boundary Conditions:

$$\boxed{\psi(x) = 0} \Rightarrow \psi(x) = A\sin kx \quad \because \cos 0 = 1$$

$$\boxed{\psi(L) = 0} \Rightarrow A\sin kL = 0 \Rightarrow \sin kL = 0 \quad \boxed{kL = n\pi \quad \text{n=1,2,3,4...}}$$

$$\boxed{\psi(x) = A\sin\frac{n\pi}{L}x}$$

Normalization:

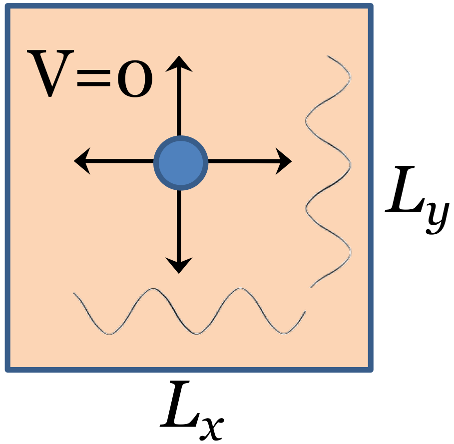
$$\boxed{\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x}$$

Recapitulation: Particle in 2-D Square-Well Potential

$$\psi(x,y) = \psi(x)\cdot\psi(y)$$

$$= \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x \cdot \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}y$$

$$= \frac{2}{L}\sin\frac{n\pi}{L}x\cdot\sin\frac{n\pi}{L}y$$



Square Box
$\Rightarrow L_x = L_y = L$

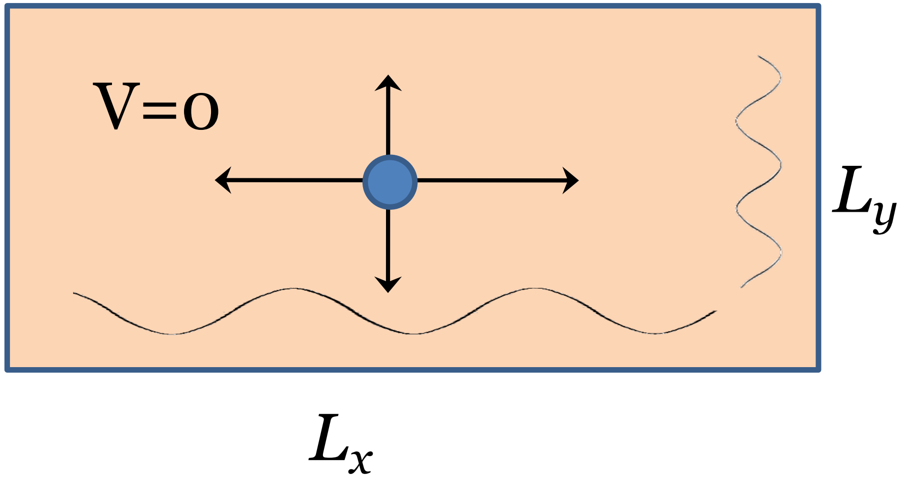
$$E_{n_x,n_y} = E_{n_x} + E_{n_y}$$

$$= \frac{n_x^2 h^2}{8mL^2} + \frac{n_y^2 h^2}{8mL^2}$$

$$= \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2\right) \qquad n_x, n_y = 1,2,3,4\ldots$$

Separation of variables

Recapitulation: Particle in 2-D Rectangular-Well Potential



$$\psi(x,y)=\psi(x)\cdot\psi(y)$$

$$=\sqrt{\frac{2}{L_x}}\sin\frac{n\pi}{L_x}x\cdot\sqrt{\frac{2}{L_y}}\sin\frac{n\pi}{L_y}y$$

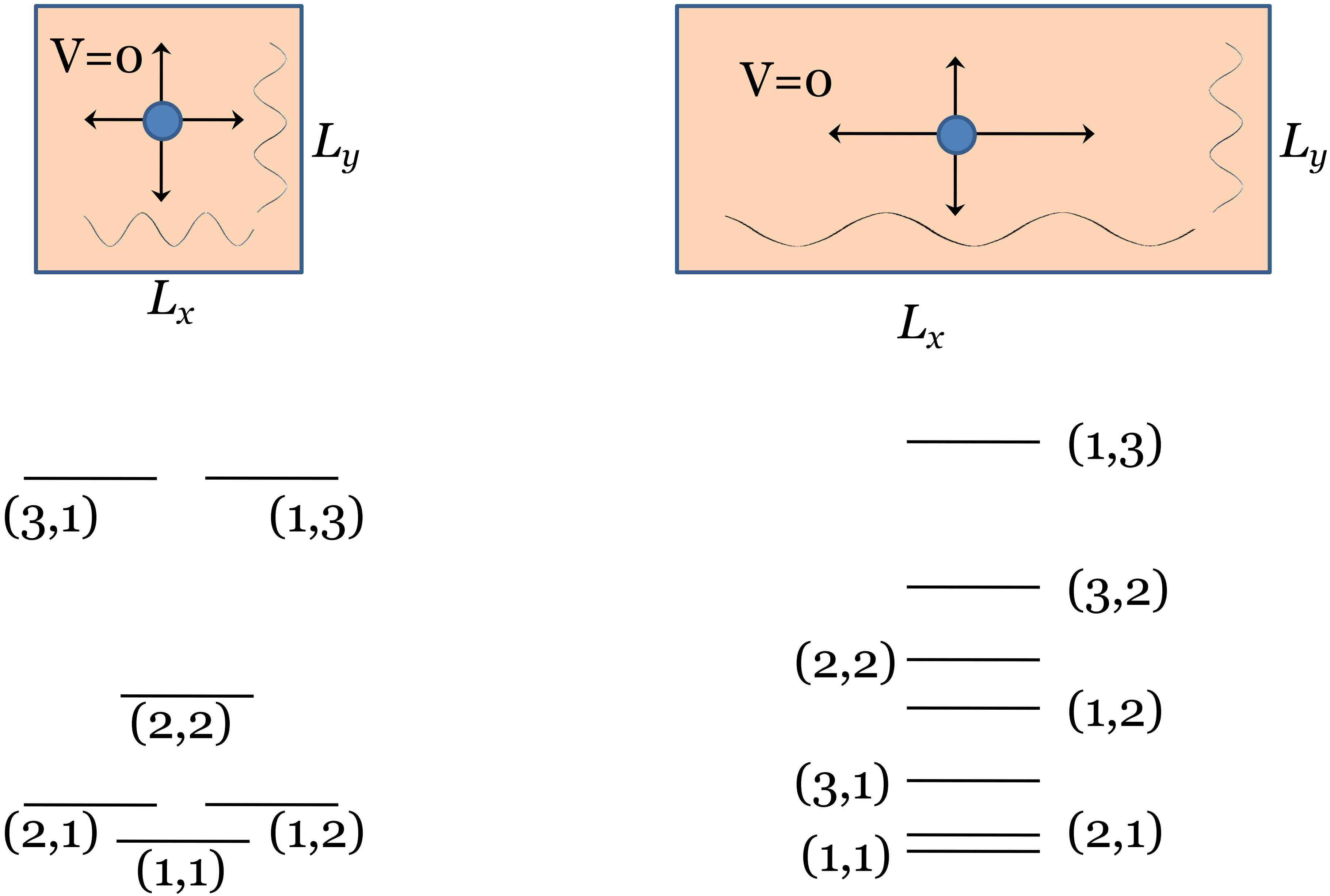
$$=\frac{2}{\sqrt{L_xL_y}}\sin\frac{n\pi}{L_x}x\cdot\sin\frac{n\pi}{L_y}y$$

$$E_{n_x,n_y}=E_{n_x}+E_{n_y}$$

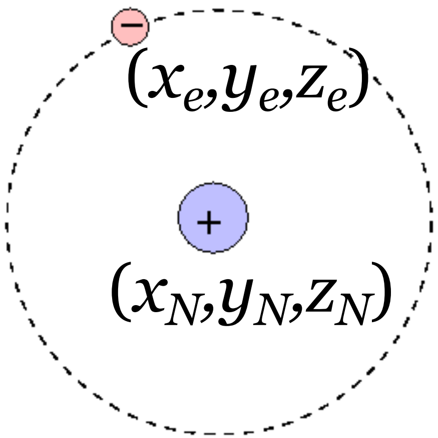
$$=\frac{n_x^2h^2}{8mL_x^2}+\frac{n_y^2h^2}{8mL_y^2}$$

$$\boxed{=\frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}\right)}\quad n_x,n_y=1,2,3,4\ldots$$

Recapitulation: Symmetry and Degeneracy



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

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

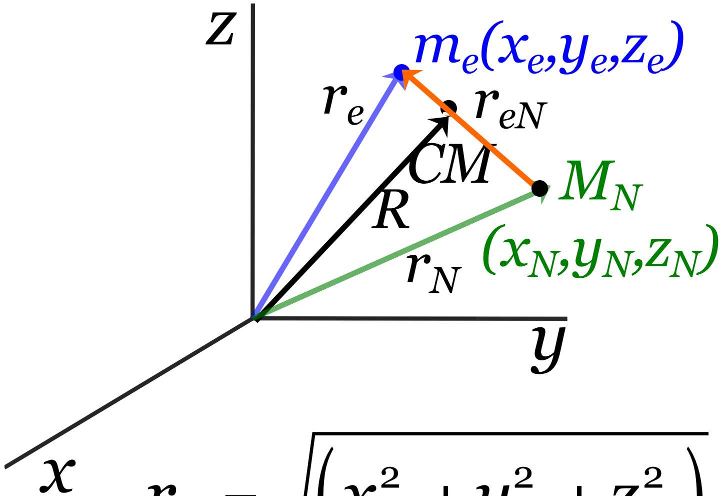
$$r_{eN} = \sqrt{(x_e - x_N)^2 + (y_e - y_N)^2 + (z_e - z_N)^2}$$

$$\Psi_{Total} = \Psi(x_N, y_N, z_N, x_e, y_e, z_e)$$

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 $\hat{\boldsymbol{H}}$ 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

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

$$\Downarrow$$

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

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

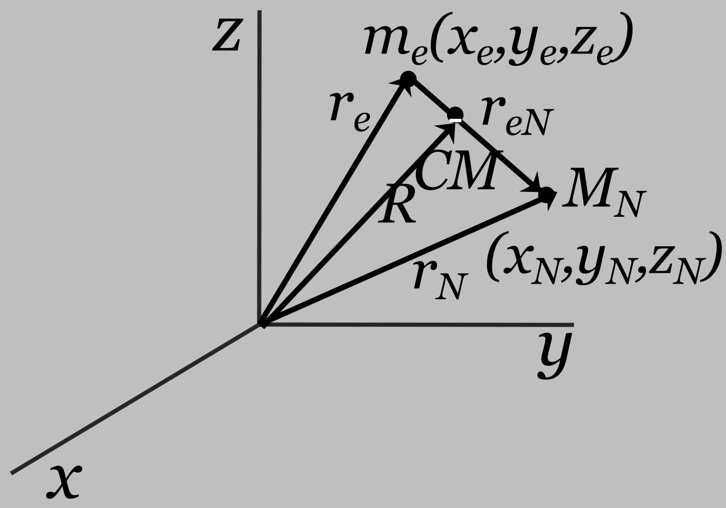
Appendix-1

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

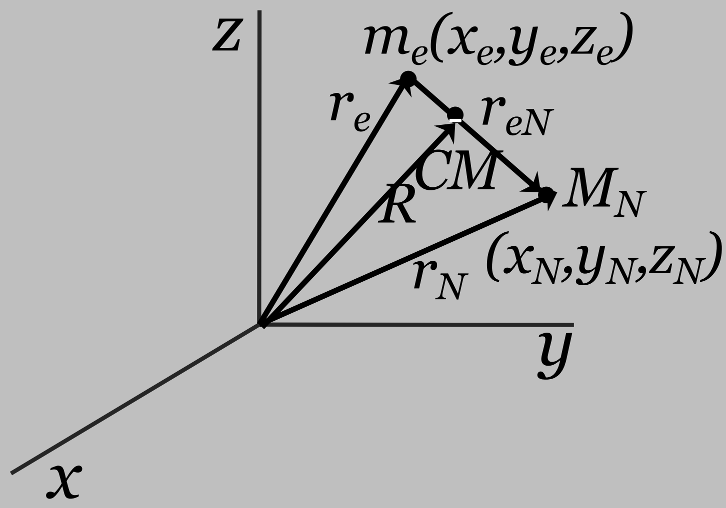
Appendix-1

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

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

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

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



Hydrogen Atom: Separation to Relative Frame

Appendix-1

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

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

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

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

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

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

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

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

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

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

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

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

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

$$E_N = \ ?$$

Hydrogen Atom: Electronic Hamiltonian

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

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

$$\psi_e \Rightarrow \psi_e(x,y,z)$$

Hydrogen Atom: Electronic Hamiltonian

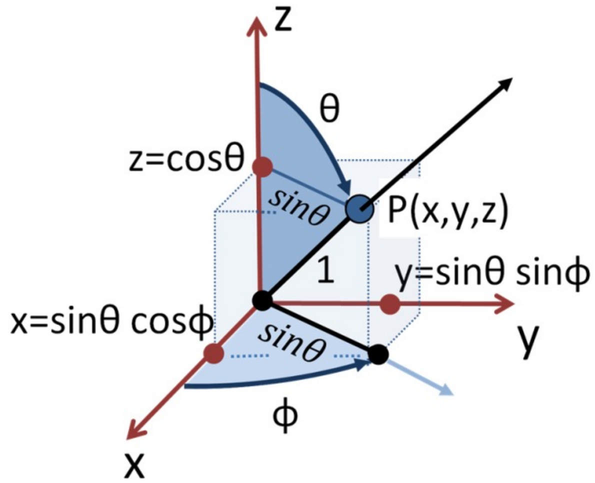
$$\widehat{H}_e \cdot \psi_e = \left(-\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{QZe^2}{r} \right) \psi_e = E_e \cdot \psi_e$$

$$\psi_e \Rightarrow \psi_e(x,y,z)$$

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

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

Spherical Polar Co-ordinates

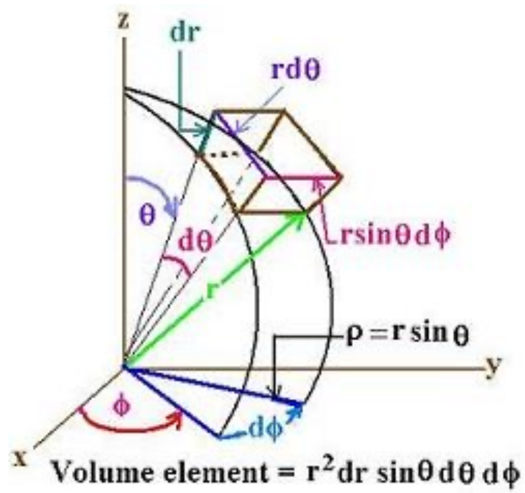


$$z = r\cos\theta$$
$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$

r: 0 to ∞

θ: 0 to π

ϕ: 0 to 2π



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

$$d\tau = dx \cdot dy \cdot dz = r^2 \cdot dr \cdot \sin\theta \cdot d\theta \cdot d\phi$$

Laplacian in Spherical Coordinates

Laplacian in Spherical Coordinates

Appendix-2

We start with the primitive definitions

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

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

and

$$z = r \cos\theta$$

and their inverses

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

$$\theta = cos^{-1}\frac{z}{r} = cos^{-1}\frac{z}{\sqrt{x^2+y^2+z^2}}$$

and

$$\phi = tan^{-1}\frac{y}{x}$$

and attempt to write (using the chain rule)

$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)_{y,z}\left(\frac{\partial}{\partial r}\right)_{\theta,\phi} + \left(\frac{\partial \theta}{\partial x}\right)_{y,z}\left(\frac{\partial}{\partial \theta}\right)_{r,\phi} + \left(\frac{\partial \phi}{\partial x}\right)_{y,z}\left(\frac{\partial}{\partial \phi}\right)_{r,\theta}$$

and

$$\frac{\partial}{\partial y} = \left(\frac{\partial r}{\partial y}\right)_{x,z}\left(\frac{\partial}{\partial r}\right)_{\theta,\phi} + \left(\frac{\partial \theta}{\partial y}\right)_{x,z}\left(\frac{\partial}{\partial \theta}\right)_{r,\phi} + \left(\frac{\partial \phi}{\partial y}\right)_{x,z}\left(\frac{\partial}{\partial \phi}\right)_{r,\theta}$$

and

$$\frac{\partial}{\partial z} = \left(\frac{\partial r}{\partial z}\right)_{x,y}\left(\frac{\partial}{\partial r}\right)_{\theta,\phi} + \left(\frac{\partial \theta}{\partial z}\right)_{x,y}\left(\frac{\partial}{\partial \theta}\right)_{r,\phi} + \left(\frac{\partial \phi}{\partial z}\right)_{x,y}\left(\frac{\partial}{\partial \phi}\right)_{r,\theta}$$

Laplacian in Spherical Coordinates

Appendix-2

The needed (above) partial derivatives are:

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \sin\theta\cos\phi \tag{1}$$

$$\left(\frac{\partial r}{\partial y}\right)_{x,z} = \sin\theta\sin\phi \tag{2}$$

$$\left(\frac{\partial r}{\partial z}\right)_{x,y} = \cos\theta \tag{3}$$

and we have as a starting point for doing the θ terms,

$$d\cos\theta = -\sin\theta d\theta = \frac{dz}{r} - \frac{z}{r^2}\frac{1}{r}(xdx + ydy + zdz)$$

Laplacian in Spherical Coordinates

Appendix-2

so that, for example

$$-\sin\theta d\theta = -\frac{z}{r^2}\frac{x}{r}dx$$

which is

$$-\sin\theta d\theta = -\frac{r\cos\theta}{r^2}\sin\theta\cos\phi dx$$

so that

$$\left(\frac{\partial\theta}{\partial x}\right)_{y,z} = \frac{\cos\theta\cos\phi}{r} \tag{4}$$

$$\left(\frac{\partial\theta}{\partial y}\right)_{x,z} = \frac{\cos\theta\sin\phi}{r} \tag{5}$$

but, for the z-equation, we have

$$-\sin\theta d\theta = \frac{dz}{r} - \frac{z}{r^2}\frac{1}{r}zdz$$

which is

$$-\sin\theta d\theta = \left(\frac{1}{r} - \frac{z^2}{r^3}\right)dz = \frac{r^2 - z^2}{r^3}dz$$

$$-\sin\theta d\theta = \left(\frac{1}{r} - \frac{z^2}{r^3}\right)dz = \frac{r^2\sin^2\theta}{r^3}dz$$

Laplacian in Spherical Coordinates

Appendix-2

so one has

$$\left(\frac{\partial\theta}{\partial z}\right)_{x,y} = -\frac{\sin\theta}{r} \tag{6}$$

Next, we have (as an example)

$$\tan\phi = \frac{\sin\phi}{\cos\phi} = \tan^{-1}\frac{y}{x}$$

so

$$\left(1 + \frac{\sin^2\phi}{\cos^2\phi}\right) d\phi = \frac{dy}{x} - \frac{y}{x^2}dx$$

or

$$\left(\frac{1}{\cos^2\phi}\right) d\phi = \frac{dy}{x} - \frac{y}{x^2}dx$$

which leads to

$$\left(\frac{\partial\phi}{\partial y}\right)_{x,z} = \frac{\cos\phi}{r\sin\theta} \tag{7}$$

and

$$\left(\frac{\partial\phi}{\partial x}\right)_{y,z} = -\frac{\sin\phi}{r\sin\theta} \tag{8}$$

Laplacian in Spherical Coordinates

Appendix-2

$$\left(\frac{\partial \phi}{\partial z}\right)_{x,y} = 0 \tag{9}$$

Given these results (above) we write

$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \left(\frac{\sin\theta}{r}\right)\frac{\partial}{\partial \theta} \tag{10}$$

and

$$\frac{\partial}{\partial y} = (\sin\theta\sin\phi)\frac{\partial}{\partial r} + \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial}{\partial \theta} + \left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial \phi} \tag{11}$$

and

$$\frac{\partial}{\partial x} = (\sin\theta\cos\phi)\frac{\partial}{\partial r} + \left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial}{\partial \theta} + \left(-\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial \phi} \tag{12}$$

From Equation 10 we form

$$\frac{\partial^2}{\partial z^2} = \cos\theta\frac{\partial\left[\cos\theta\frac{\partial}{\partial r} - \left(\frac{\sin\theta}{r}\right)\frac{\partial}{\partial\theta}\right]}{\partial r} - \left(\frac{\sin\theta}{r}\right)\frac{\partial\left(\cos\theta\frac{\partial}{\partial r} - \left(\frac{\sin\theta}{r}\right)\frac{\partial}{\partial\theta}\right]}{\partial\theta} \tag{13}$$

while from Equation 11 we obtain

$$\begin{aligned}\frac{\partial^2}{\partial y^2} &= (\sin\theta\sin\phi)\frac{\partial\left[\sin\theta\sin\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial}{\partial\theta} + \left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\partial r\right]}{\partial r}\\ &+ \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial\left[\sin\theta\sin\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial}{\partial\theta} + \left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\right]}{\partial\theta}\\ &+ \left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial\left[\sin\theta\sin\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial}{\partial\theta} + \left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\right]}{\partial\phi}\end{aligned} \tag{14}$$

Laplacian in Spherical Coordinates

Appendix-2

and from Equation 12 we obtain

$$\frac{\partial^2}{\partial x^2} = (\sin\theta\cos\phi)\frac{\partial\left[\sin\theta\cos\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial}{\partial\theta} - \left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\right]}{\partial r}$$
$$+ \left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial\left[\sin\theta\cos\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial}{\partial\theta} - \left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\right]}{\partial\theta}$$
$$- \left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial\left[\sin\theta\cos\phi\frac{\partial}{\partial r} + \left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial}{\partial\theta} - \left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}\right]}{\partial\phi} \quad (15)$$

Expanding, we have

$$\frac{\partial^2}{\partial z^2} = \cos^2\theta\frac{\partial^2}{\partial r^2} + \frac{\cos\theta\sin\theta}{r^2}\frac{\partial}{\partial\theta} - \frac{\sin\theta\cos\theta}{r}\frac{\partial^2}{\partial r\partial\theta}$$
$$-\left(\frac{\sin\theta}{r}\right)\left(-\sin\theta\frac{\partial}{\partial r} - \cos\theta\frac{\partial}{\partial\theta}\right) - \frac{\sin\theta\cos\theta}{r^2}\frac{\partial}{\partial\theta} + \left(\frac{\sin\theta}{r}\right)^2\frac{\partial^2}{\partial\theta^2} \quad (16)$$

while for the y-equation we have

$$\frac{\partial^2}{\partial y^2} = \sin^2\theta\sin^2\phi\frac{\partial^2}{\partial r^2} \quad (17)$$

$$+\sin\theta\sin\phi\left[+\left(\frac{\cos\theta\sin\phi}{r^2}\right)\frac{\partial}{\partial\theta} + \left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial^2}{\partial r\partial\theta}\right] \quad (18)$$

Laplacian in Spherical Coordinates

Appendix-2

$$+\sin\theta\sin\phi\left[\left(-\frac{\cos\phi}{r^2\sin\theta}\right)\frac{\partial}{\partial\phi}+\left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial r\partial\phi}\right] \quad (19)$$

$$+\left(\frac{\cos\theta\sin\phi}{r}\right)\left[\cos\theta\sin\phi\frac{\partial}{\partial r}+\sin\theta\sin\phi\frac{\partial^2}{\partial r\partial\theta}\right] \quad (20)$$

$$+\left(\frac{\cos\theta\sin\phi}{r}\right)\left[-\left(\frac{\sin\theta\sin\phi}{r}\right)\frac{\partial}{\partial\theta}+\left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial^2}{\partial\theta^2}\right] \quad (21)$$

$$+\left(\frac{\cos\theta\sin\phi}{r}\right)\left[-\left(\frac{\cos\phi\cos\theta}{r\sin^2\theta}\right)\frac{\partial}{\partial\phi}+\left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial\phi\partial\theta}\right] \quad (22)$$

$$+\left(\frac{\cos\phi}{r\sin\theta}\right)\left[\sin\theta\cos\phi\frac{\partial}{\partial r}+\sin\theta\sin\phi\frac{\partial^2}{\partial r\partial\phi}\right] \quad (23)$$

$$+\left(\frac{\cos\phi}{r\sin\theta}\right)\left[+\left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial}{\partial\theta}+\left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial^2}{\partial\theta\partial\phi}\right] \quad (24)$$

$$+\left(\frac{\cos\phi}{r\sin\theta}\right)\left[-\left(\frac{\sin\phi\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}+\left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial\phi^2}\right] \quad (25)$$

Laplacian in Spherical Coordinates

Appendix-2

and finally

$$\frac{\partial^2}{\partial x^2} = (\sin\theta\cos\phi)\sin\theta\cos\phi\frac{\partial^2}{\partial r^2}$$

$$+(\sin\theta\cos\phi)\left[-\left(\frac{\cos\theta\cos\phi}{r^2}\right)\frac{\partial}{\partial\theta}+\left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial^2}{\partial\theta\partial r}\right] \tag{26}$$

$$-(\sin\theta\cos\phi)\left[-\left(\frac{\sin\phi}{r^2\sin\theta}\right)\frac{\partial}{\partial\phi}+\left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial\phi\partial r}\right] \tag{27}$$

$$+\left(\frac{\cos\theta\cos\phi}{r}\right)\left[\cos\theta\cos\phi\frac{\partial}{\partial r}+\sin\theta\cos\phi\frac{\partial^2}{\partial r\partial\theta}\right] \tag{28}$$

$$+\left(\frac{\cos\theta\cos\phi}{r}\right)\left[-\left(\frac{\sin\theta\cos\phi}{r}\right)\frac{\partial}{\partial\theta}+\left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial^2}{\partial\theta^2}\right] \tag{29}$$

$$+\left(\frac{\cos\theta\cos\phi}{r}\right)\left[+\left(\frac{\sin\phi}{r\sin^2\theta}\right)\frac{\partial}{\partial\phi}-\left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial\phi\partial\theta}\right] \tag{30}$$

$$-\left(\frac{\sin\phi}{r\sin\theta}\right)\left[\sin\theta\sin\phi\frac{\partial}{\partial r}+\sin\theta\cos\phi\frac{\partial^2}{\partial r\partial\phi}\right] \tag{31}$$

$$-\left(\frac{\sin\phi}{r\sin\theta}\right)\left[-\left(\frac{\cos\theta\sin\phi}{r}\right)\frac{\partial}{\partial\theta}+\left(\frac{\cos\theta\cos\phi}{r}\right)\frac{\partial^2}{\partial\theta\partial\phi}\right] \tag{32}$$

$$-\left(\frac{\sin\phi}{r\sin\theta}\right)\left[-\left(\frac{\cos\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi}-\left(\frac{\sin\phi}{r\sin\theta}\right)\frac{\partial^2}{\partial\phi^2}\right] \tag{33}$$

Now, one by one, we expand completely each of these three terms. We have

$$\frac{\partial^2}{\partial z^2} = \cos^2\theta\frac{\partial^2}{\partial r^2} \tag{34}$$

$$+\frac{\cos\theta\sin\theta}{r^2}\frac{\partial}{\partial\theta} \tag{35}$$

$$-\frac{\sin\theta\cos\theta}{r}\frac{\partial^2}{\partial r\partial\theta} \tag{36}$$

$$+\left(\frac{\sin^2\theta}{r}\right)\frac{\partial}{\partial r} \tag{37}$$

$$-\left(\frac{\sin\theta\cos\theta}{r}\right)\frac{\partial^2}{\partial r\partial\theta} \tag{38}$$

$$+\frac{\sin\theta\cos\theta}{r^2}\frac{\partial}{\partial\theta} \tag{39}$$

$$+\left(\frac{\sin^2\theta}{r^2}\right)\frac{\partial^2}{\partial\theta^2} \tag{40}$$

Laplacian in Spherical Coordinates

Appendix-2

and, for the y-equation:

$$\frac{\partial^2}{\partial y^2} = \sin^2\theta \sin^2\phi \frac{\partial^2}{\partial r^2} \tag{41}$$

$$(18) \rightarrow + \left(\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}\right)\frac{\partial}{\partial\theta} \tag{42}$$

$$+ \left(\frac{\cos\theta\sin\theta\sin^2\phi}{r}\right)\frac{\partial^2}{\partial r\partial\theta} \tag{43}$$

$$(19) \rightarrow - \left(\frac{\sin\phi\cos\phi}{r^2}\right)\frac{\partial}{\partial\phi} \tag{44}$$

$$+ \left(\frac{\cos\phi\sin\phi}{r}\right)\frac{\partial^2}{\partial r\partial\phi} \tag{45}$$

$$(20) \rightarrow + \left(\frac{\cos^2\theta\sin^2\phi}{r}\right)\frac{\partial}{\partial r} \tag{46}$$

$$+ \left(\frac{\cos\theta\sin\theta\sin^2\phi}{r}\right)\frac{\partial^2}{\partial r\partial\theta} \tag{47}$$

$$- \left(\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}\right)\frac{\partial}{\partial\theta} \tag{48}$$

$$(21) \rightarrow + \left(\frac{\cos^2\theta\sin^2\phi}{r^2}\right)\frac{\partial^2}{\partial\theta^2} \tag{49}$$

$$- \left(\frac{\cos^2\theta\cos\phi\sin\phi}{r\sin^2\theta}\right)\frac{\partial}{\partial\phi} \tag{50}$$

$$+ \left(\frac{\cos\theta\cos\phi\sin\phi}{r^2\sin\theta}\right)\frac{\partial^2}{\partial\phi\partial\theta} \tag{51}$$

$$(22) \rightarrow + \left(\frac{\cos^2\phi}{r}\right)\frac{\partial}{\partial r} \tag{52}$$

$$+ \left(\frac{\cos\phi\sin\phi}{r}\right)\frac{\partial^2}{\partial r\partial\phi} \tag{53}$$

Laplacian in Spherical Coordinates

Appendix-2

$$+\left(\frac{\cos^2\phi\cos\theta}{r^2\sin\theta}\right)\frac{\partial}{\partial\theta} \tag{54}$$

$$(24)\rightarrow+\left(\frac{\cos\theta\cos\phi\sin\phi}{r^2\sin\theta}\right)\frac{\partial^2}{\partial\theta\partial\phi} \tag{55}$$

$$(25)\rightarrow-\left(\frac{\cos^2\phi\sin\phi}{r\sin^2\theta}\right)\frac{\partial}{\partial\phi} \tag{56}$$

$$+\left(\frac{\cos^2\phi}{r^2\sin^2\theta}\right)\frac{\partial^2}{\partial\phi^2} \tag{57}$$

and finally, for the x-equation, we have

$$\frac{\partial^2}{\partial x^2}=\sin^2\theta\cos^2\phi\frac{\partial^2}{\partial r^2} \tag{58}$$

$$(26)\rightarrow-\left(\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}\right)\frac{\partial}{\partial\theta} \tag{59}$$

$$(26)\rightarrow+\left(\frac{\sin\theta\cos\theta\cos^2\phi}{r}\right)\frac{\partial^2}{\partial\theta\partial r} \tag{60}$$

$$\left(\frac{\cos\phi\sin\phi}{r^2}\right)\frac{\partial}{\partial\phi} \tag{61}$$

$$-\left(\frac{\sin\phi\cos\phi}{r}\right)\frac{\partial^2}{\partial\phi\partial r} \tag{62}$$

Laplacian in Spherical Coordinates

Appendix-2

$$(27) \rightarrow +\left(\frac{\cos^2\theta\cos^2\phi}{r}\right)\frac{\partial}{\partial r} \tag{63}$$

$$+\left(\frac{\sin\theta\cos\theta\cos^2\phi}{r}\right)\frac{\partial^2}{\partial r\partial\theta} \tag{64}$$

$$(27) \rightarrow -\left(\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}\right)\frac{\partial}{\partial\theta} \tag{65}$$

$$+\left(\frac{\cos^2\theta\cos^2\phi}{r^2}\right)\frac{\partial^2}{\partial\theta^2} \tag{66}$$

$$(28) \rightarrow +\left(\frac{\cos\theta\cos\phi}{r}\right)\left(\frac{\cos\phi\sin\phi}{r\sin\theta}\right)\frac{\partial}{\partial\phi} \tag{67}$$

$$-\left(\frac{\sin\phi\cos\phi\cos\theta}{r^2\sin\theta}\right)\frac{\partial^2}{\partial\phi\partial\theta} \tag{68}$$

$$(29) \rightarrow -\left(\frac{\sin^2\phi}{r}\right)\frac{\partial}{\partial r} \tag{69}$$

$$-\left(\frac{\sin\phi\cos\phi}{r}\right)\frac{\partial^2}{\partial r\partial\phi} \tag{70}$$

$$(31) \rightarrow +\left(\frac{\cos\theta\sin^2\phi}{r^2\sin\theta}\right)\frac{\partial}{\partial\theta} \tag{71}$$

$$-\left(\frac{\cos\theta\sin\phi\cos\phi}{r^2\sin\theta}\right)\frac{\partial^2}{\partial\theta\partial\phi} \tag{72}$$

$$(32) \rightarrow +\left(\frac{\sin\phi\cos\phi}{r\sin^2\theta}\right)\frac{\partial}{\partial\phi} \tag{73}$$

$$+\left(\frac{\sin^2\phi}{r^2\sin^2\theta}\right)\frac{\partial^2}{\partial\phi^2} \tag{74}$$

Laplacian in Spherical Coordinates

Appendix-2

Gathering terms as coefficients of partial derivatives, we obtain (from Equations 34, 41 and 58)

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

and (from Equations 35, 38, 42, 48, 54, 59, 65, and 71)

$$\frac{\partial}{\partial\theta}\left(+\frac{\cos\theta\sin\theta}{r^2} + \frac{\sin\theta\cos\theta}{r^2} - \frac{\sin\theta\cos\theta\sin^2\phi}{r^2} - \frac{\sin\theta\cos\theta\sin^2\phi}{r^2} + \frac{\cos^2\phi\cos\theta}{r^2\sin\theta}\right.$$
$$\left. - \frac{\sin\theta\cos\theta\cos^2\phi}{r^2} - \frac{\sin\theta\cos\theta\cos^2\phi}{r^2} + \frac{\cos\theta\sin^2\phi}{r^2\sin\theta}\right)$$
$$\to \frac{\cos\theta}{r^2\sin\theta}\frac{\partial}{\partial\theta} \tag{75}$$

while we obtain from Equations 40, 49, and 66:

$$\frac{\partial^2}{\partial\theta^2}\left(\frac{\sin^2\theta}{r^2} + \frac{\cos^2\theta\sin^2\phi}{r^2} + \frac{\cos^2\theta\cos^2\phi}{r^2}\right) \to \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} \tag{76}$$

From Equations 37, 46, 52, 63, 69,

$$\frac{\partial}{\partial r}\left(+\frac{\sin^2\theta}{r} + \frac{\cos^2\theta\sin^2\phi}{r} + \frac{\cos^2\phi}{r} + \frac{\cos^2\theta\cos^2\phi}{r} - \frac{\sin^2\phi}{r}\right) \to \frac{2}{r}\frac{\partial}{\partial r} \tag{77}$$

From Equations 44, 50, 56, 61, 67 and 73 we obtain

$$\frac{\partial}{\partial\phi}\left(-\frac{\sin\phi\cos\phi}{r^2} - \frac{\cos^2\theta\cos\phi\sin\phi}{r\sin^2\theta} - \frac{\cos^2\theta\cos\phi\sin\phi}{r\sin^2\theta} + \frac{\cos\phi\sin\phi}{r^2} + \left(\frac{\cos\theta\cos\phi}{r}\right)\right.$$
$$\left. + \left(\frac{\cos\theta\cos^2\phi\sin\phi}{r^2\sin\theta}\right) + \frac{\sin\phi\cos\phi}{r\sin^2\theta}\right) \to 0 \tag{78}$$

Laplacian in Spherical Coordinates

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

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

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

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

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

Separation of variables

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

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

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

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

Angular equation

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

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

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

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

The three variables r, θ and ϕ are separated

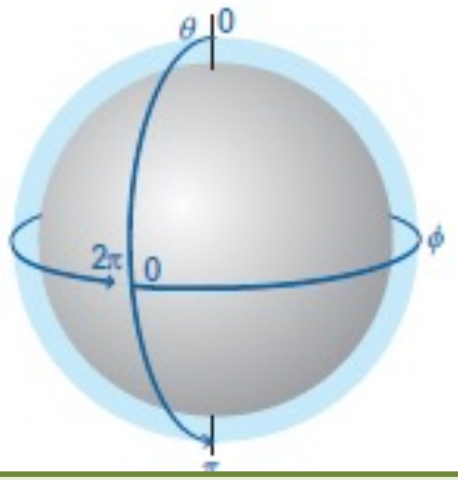
Solution to ϕ part

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

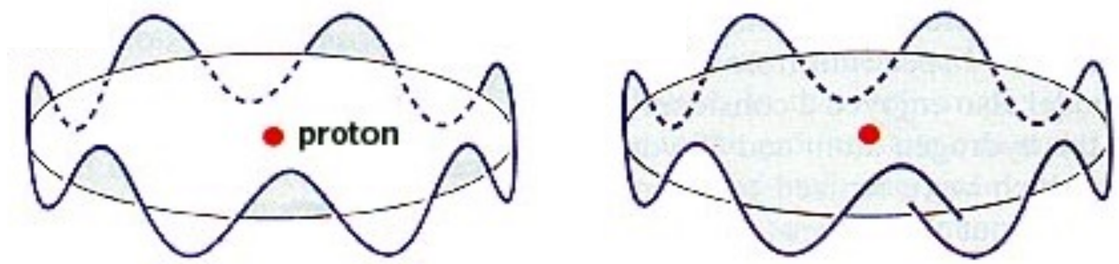
$$\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2\Phi(\phi)$$

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 continuous

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

Periodic Boundary Condition

Solution to ϕ part

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

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

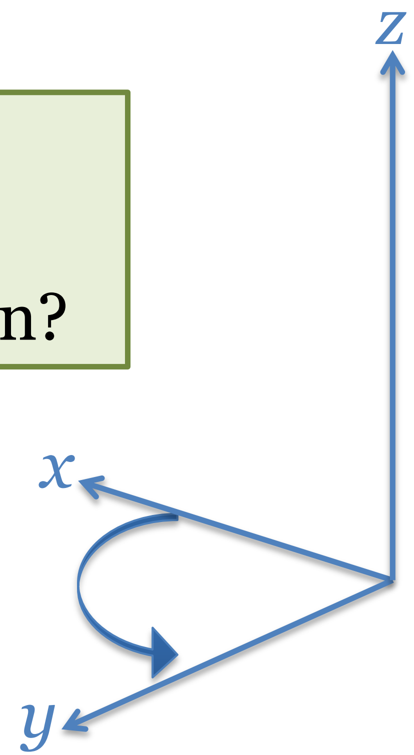
$$e^{im(2\pi)} = 1 \quad \text{and} \quad e^{-im(2\pi)} = 1$$

$$\cos(2\pi m) \pm i \sin(2\pi m) = 1$$

- True only if m=0, ±1, ±2, ±3, ±4,....
- What kind of information does Φ contain?

Change in ϕ: Circular motion in xy plane

z – component of angular momentum?



Angular momentum: from classical to quantum picture

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

L_z

$$\widehat{p_y} = \frac{\hbar}{i}\frac{\partial}{\partial y}; \qquad \widehat{p_x} = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\therefore \widehat{L_z} = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \longrightarrow \longrightarrow \boxed{\widehat{L_z} = \frac{\hbar}{i}\frac{\partial}{\partial \phi}}$$

Is Φ an eigenfunction?

Moment of truth

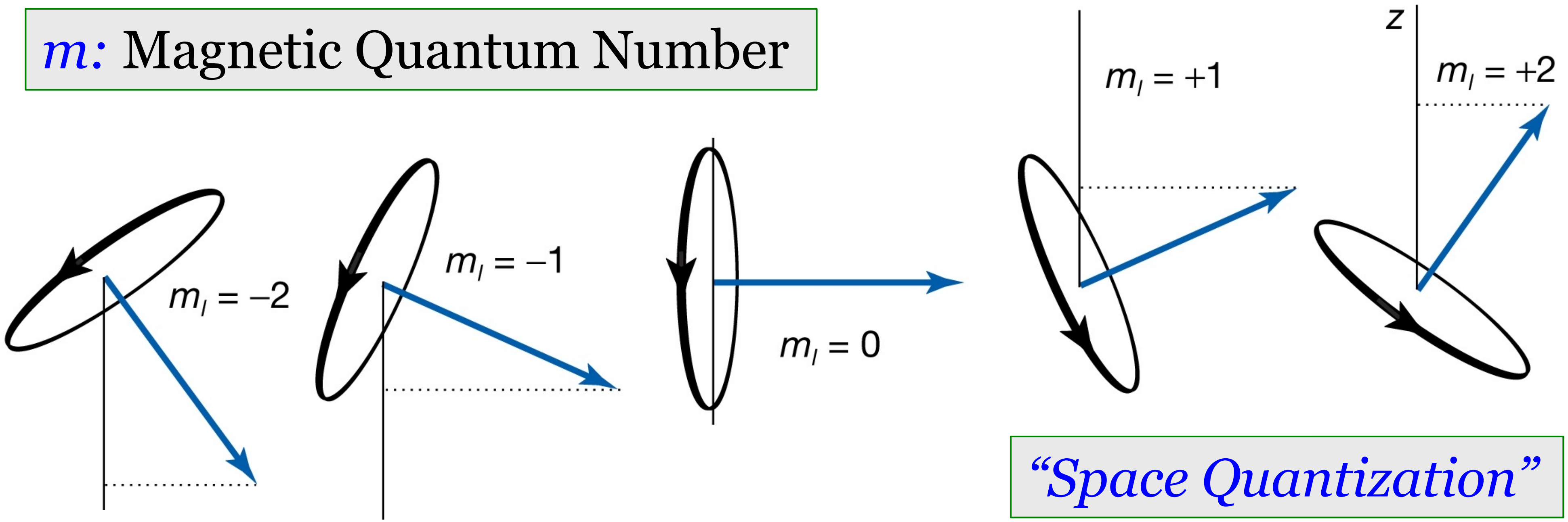
$$\widehat{L_z} = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$

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

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

z-component of angular momentum

m: Magnetic Quantum Number



"Space Quantization"

The Θ and the R part

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(\frac{QZe^2}{r}+E_e\right)R(r)-\beta R(r)=0$$

Solve to get $R(r)$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)-\frac{m^2}{\sin^2\theta}\Theta(\theta)+\beta\Theta(\theta)=0$$

Solve to get $\Theta(\theta)$

**Need serious mathematical skill to solve these two equations.
We only look at solutions**

The Θ part

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)-\frac{m^2}{\sin^2\theta}\Theta(\theta)+\beta\Theta(\theta)=0$$

Solution to $\Theta(\theta)$:

$l=0,1,2,3\ldots$

$P_l^m(\cos\theta)$:Associated Legendre Polynomials

New quantum number 'l' : orbital / Azimuthal quantum number

Restriction on $m \leq l$
is due to this equation

The angular (Θ·Φ) part

The angular part of the solution

$Y_l^m(\theta,\phi) \Rightarrow \Theta(\theta)\cdot\Phi(\phi)$ are called spherical harmonics

$$Y_l^m(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}$$

l=0,1,2,3…

m=0, ±1, ±2, ±3… and $|m| \le l$

The *R* part

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(\frac{QZe^2}{r}+E_e\right)R(r)-\beta R(r)=0$$

Solution to R(r) are

$$a=\frac{\hbar^2}{Q\mu e^2}=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

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

Restriction on $l<n$

Where $L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$ are called associated *Laguerre* functions

The new quantum number is ‘*n*’ called principal quantum number

Energy of the Hydrogen Atom

$$E_n = -\frac{2Q^2 Z^2 \mu e^4}{\hbar^2 n^2} = -\frac{Z^2 \mu e^4}{8\varepsilon_o^2 h^2 n^2} = -\frac{Z^2 e^4}{8\pi\varepsilon_o a_o n^2}\left(\mu \approx m_e\right)$$

$$E_n = \frac{-13.6eV}{n^2}$$

Energy is dependent only on '*n*'

Energy obtained by full quantum mechanical treatment is equal to Bohr energy

Potential energy term is only dependent on the ***Radial*** part and has no contribution from the ***Angular*** parts

Quantum Numbers of Hydrogen Atom

n	**Principal Quantum number** Specifies the energy of the electron
l	**Orbital Angular Momentum Quantum number** Specifies the magnitude of the electron's orbital angular momentum
m	**Z-component of Angular Momentum Quantum number** Specifies the orientation of the electron's orbital angular momentum
s	**Orbital Angular Momentum Quantum number** Specifies the orientation of the electron's spin angular momentum