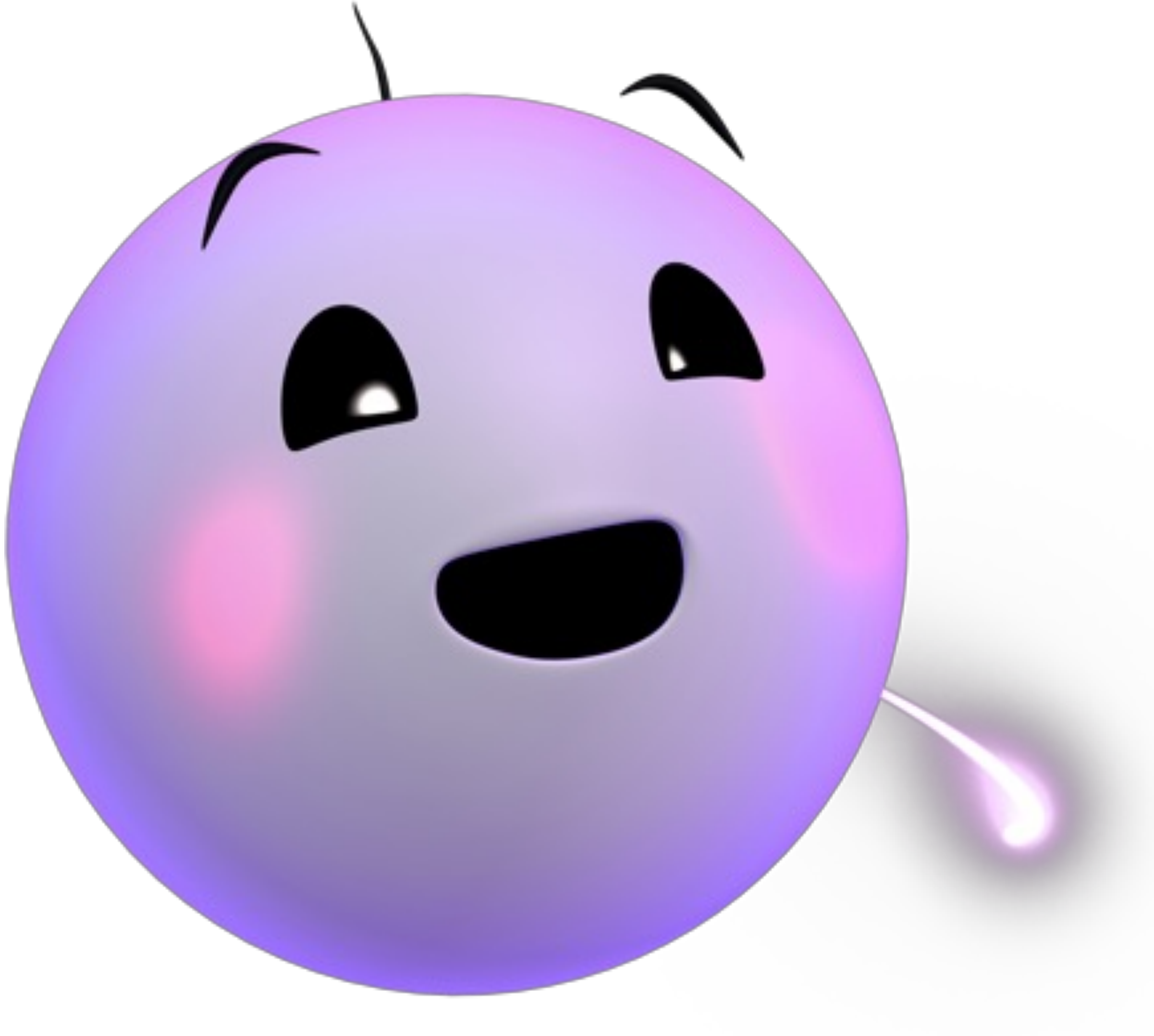
Lecture 5: Hydrogen Atom



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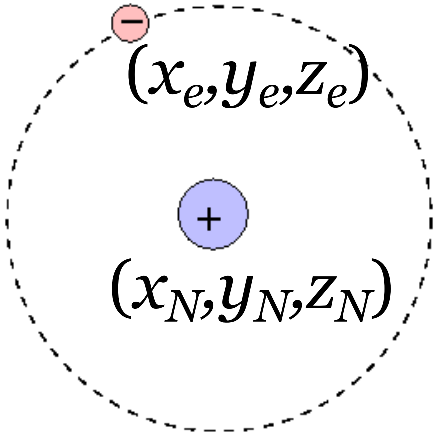
Hydrogen Atom



Two particle central-force problem

Completely solvable – a rare example!

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon_0}\frac{Z_N Z_e e^2}{r_{eN}}$$

$$\nabla_N^2 = \frac{\partial^2}{\partial x_N^2} + \frac{\partial^2}{\partial y_N^2} + \frac{\partial^2}{\partial z_N^2} \qquad \nabla_e^2 = \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}$$

Hydrogen Atom

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

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{QZe^2}{r_{eN}}$$

with $\boxed{Z_N = Z}$ $\boxed{Z_e = 1}$ and $\boxed{\frac{1}{4\pi\varepsilon_o} = Q}$

Schrödinger Equation

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

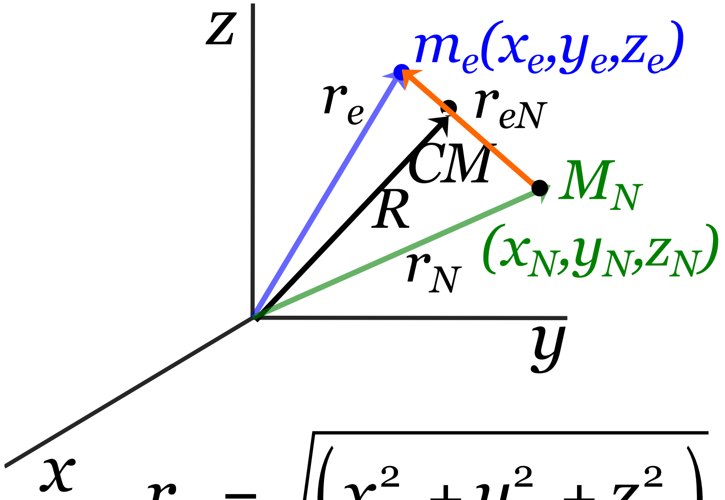
$$r_{eN} = \sqrt{(x_e - x_N)^2 + (y_e - y_N)^2 + (z_e - z_N)^2}$$

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

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



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

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

$$x = x_e - x_N$$

$$y = y_e - y_N$$

$$z = z_e - z_N$$

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

$$= \sqrt{\left(x^2 + y^2 + z^2\right)}$$

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

$$Y = \frac{m_e y_e + m_N y_n}{m_e + m_N}$$

$$Z = \frac{m_e z_e + m_N z_n}{m_e + m_N}$$

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

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 of CM motion

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

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

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

Free particle!
Kinetic energy of the atom

$$E_N = \frac{\hbar^2 k^2}{2M}$$

Hydrogen Atom: Electronic Hamiltonian

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

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

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

Hydrogen Atom: Electronic Hamiltonian

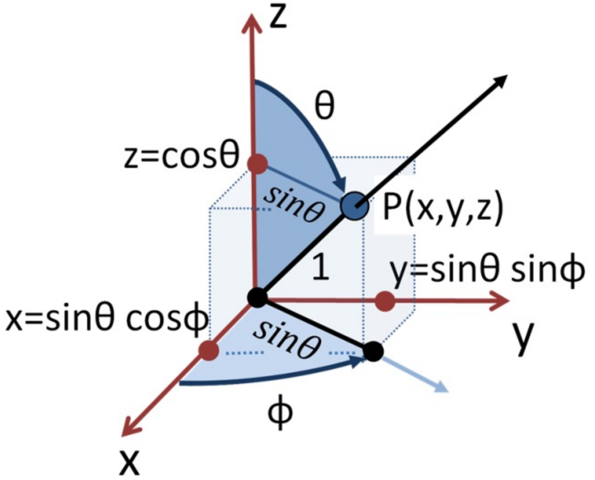
$$\widehat{H}_e \cdot \psi_e = \left(-\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{QZe^2}{r} \right) \psi_e = E_e \cdot \psi_e$$

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

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

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

Spherical Polar Co-ordinates

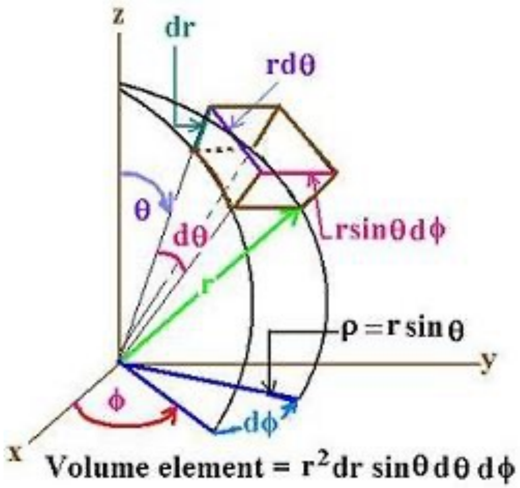


$$z = r\cos\theta$$
$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$

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

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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,

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

Laplacian in Spherical Coordinates

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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

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

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

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

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

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

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and from Equation 12 we obtain

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

Expanding, we have

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

while for the y-equation we have

$$\frac{\partial^2}{\partial y^2} = \sin^2\theta\sin^2\phi\frac{\partial^2}{\partial r^2} \tag{17}$$

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

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

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

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

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

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

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

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

Laplacian in Spherical Coordinates

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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

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

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

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

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

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

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

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

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and, for the y-equation:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

and finally, for the x-equation, we have

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Laplacian in Spherical Coordinates

Appendix-2

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

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

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

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

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

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

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

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

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

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

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

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

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

Separation of variables

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

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

$$\psi_e(r,\theta,\phi)\Rightarrow R(r)\cdot\Theta(\theta)\cdot\Phi(\phi)$$

$$\psi_e\Rightarrow R\cdot\Theta\cdot\Phi$$

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

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

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

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

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

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

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

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

Separation of variables

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

Rearrange

Radial **Angular**

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

$$=\beta$$

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

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

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

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

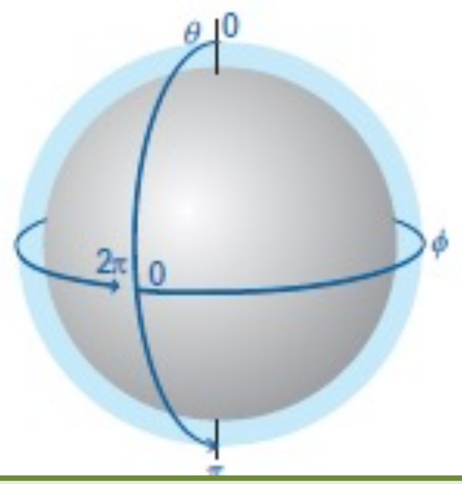
Solution to ϕ part

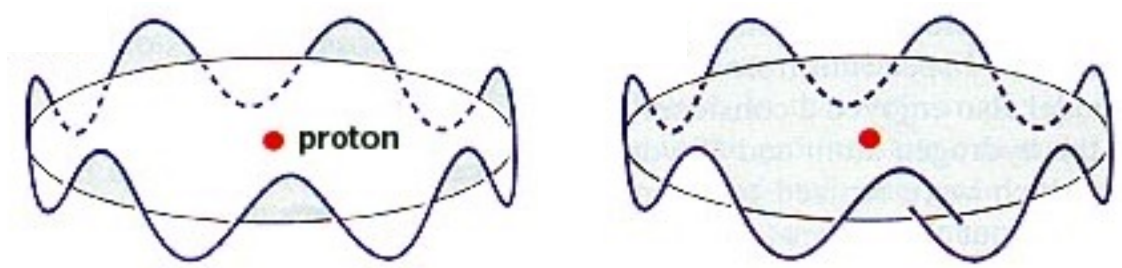
$$\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}+m^2=0$$

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

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

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

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

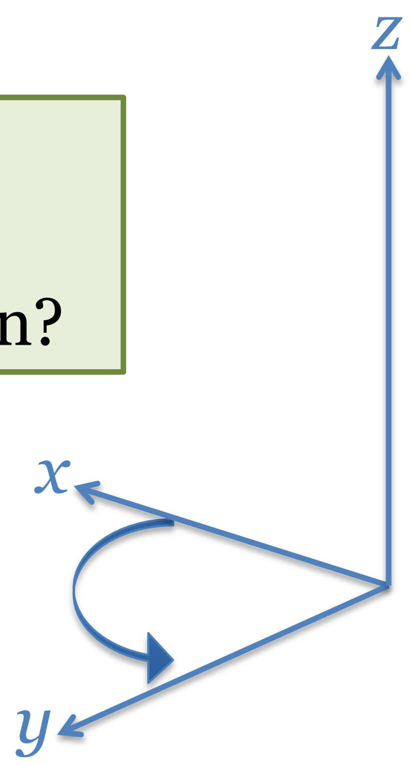
$$e^{im(2\pi)} = 1 \quad \text{and} \quad e^{-im(2\pi)} = 1$$

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

- 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

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

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

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

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

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

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

Is Φ an eigenfunction?

Moment of truth

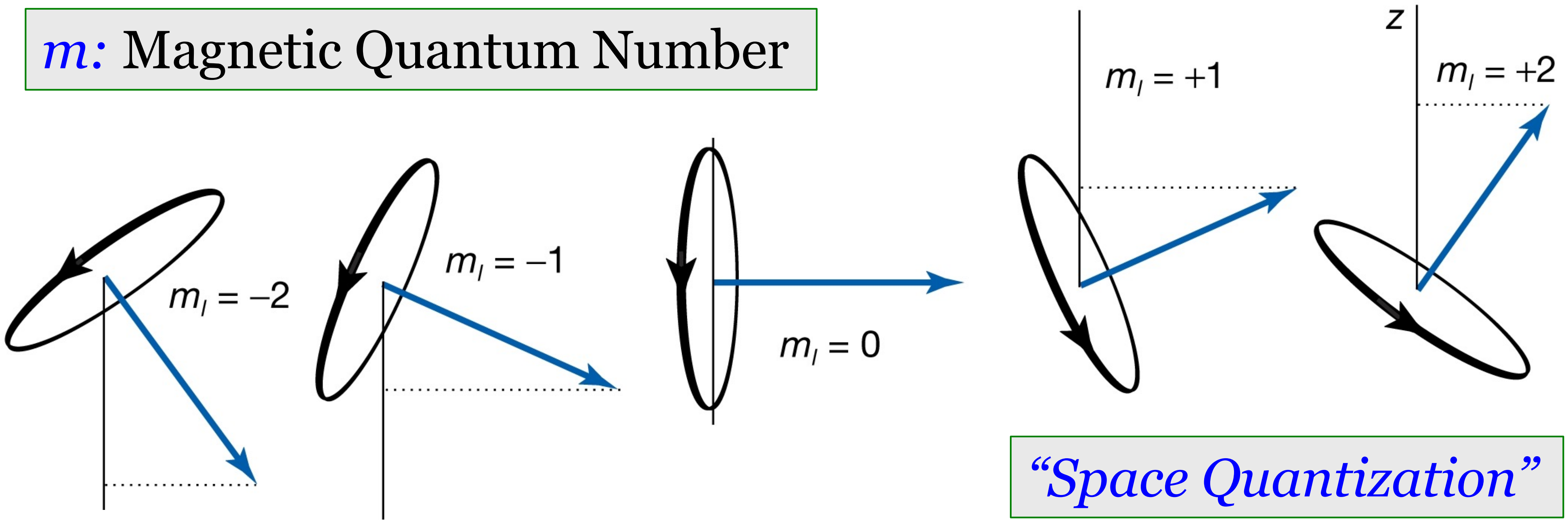
$$\widehat{L_z} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

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

$$\widehat{L_z}\Phi = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\Phi = \frac{\hbar}{i}\, im\,\Phi = \boxed{m\hbar}\,\Phi$$

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 $\Theta(\theta)$:

$$P_l^m(\cos\theta)=\frac{(-1)^m}{2^l l!}(1-\cos^2\theta)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(\cos^2\theta-1)^l$$

l=0,1,2,3...

$$P_l^{-m}(\cos\theta)=(-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(\cos\theta) \qquad \text{with} \quad \beta=l(l+1)$$

$P_l^m(\cos\theta)$: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 $|m|\leq l$

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

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

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

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