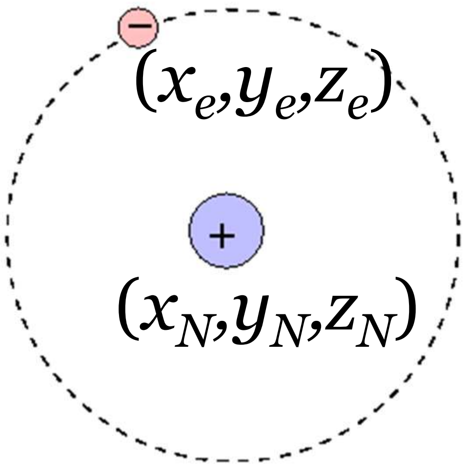
Hydrogen Atom



Two particle central-force problem

Completely solvable – a rare example!

$$\widehat{H} = \widehat{T}_N + \widehat{T}_e + \widehat{V}_{N\text{-}e}$$

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

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

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

Hydrogen Atom

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

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

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

Schrodinger Equation

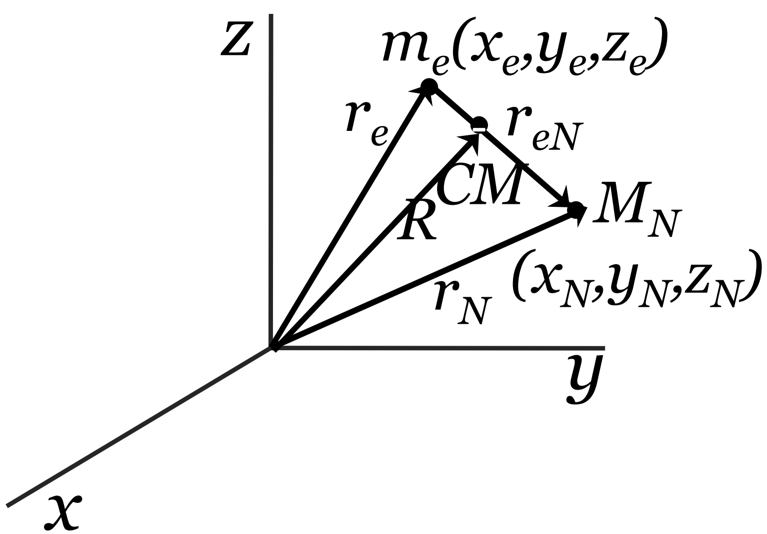
$$\left[-\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{QZe^2}{r_{eN}}\right]\Psi_{Total} = E_{Total}\cdot\Psi_{Total}$$

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

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



$$x=x_e-x_N$$

$$y=y_e-y_N$$

$$z=z_e-z_N$$

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

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

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

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

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

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

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

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

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

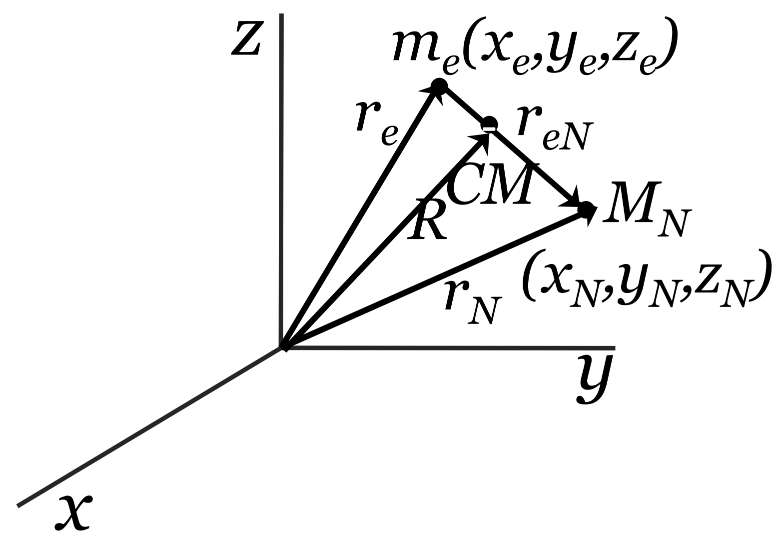
Appendix-1

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

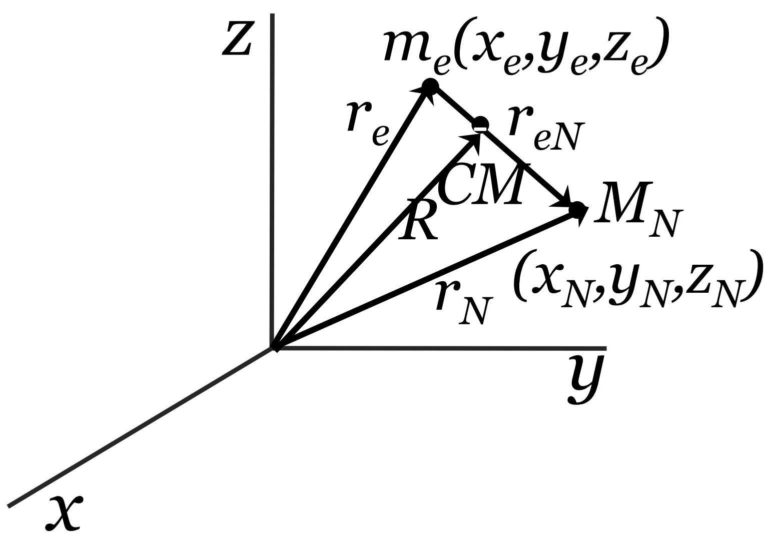
Appendix-1

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

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

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

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



Hydrogen Atom: Separation to Relative Frame

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

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

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

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

$$\dot{r}_e = \frac{dr_e}{dt} \qquad \dot{r}_N = \frac{dr_N}{dt} \qquad \dot{r} = \frac{dr}{dt} \qquad \dot{R} = \frac{dR}{dt}$$

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

Hydrogen Atom: Separation to Relative Frame

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

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

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

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

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

$$-\frac{\hbar^2}{2M}\nabla_R^2=\widehat{H}_N \qquad -\frac{\hbar^2}{2\mu}\nabla_r^2-\frac{QZe^2}{r}=\widehat{H}_e$$

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

Free particle!
Kinetic energy of the atom

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

Hydrogen Atom: Electronic Hamiltonian

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

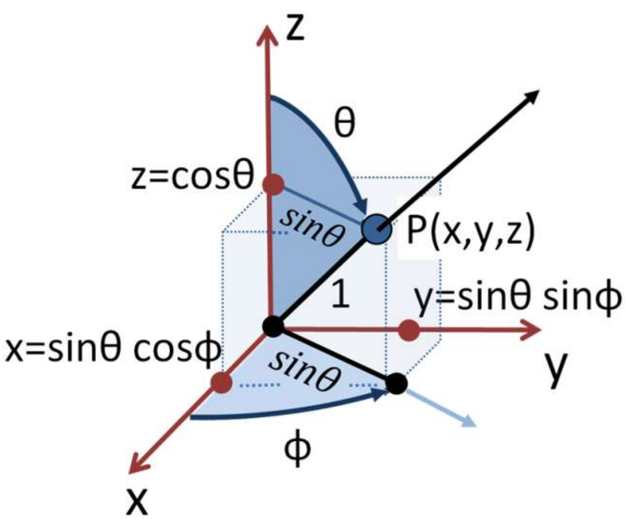
$$\psi_e \Rightarrow \psi_e(x,y,z)$$

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)\psi_e(x,y,z) - \frac{QZe^2}{\underbrace{\sqrt{\left(x^2+y^2+z^2\right)}}_{r}}\psi_e(x,y,z)$$

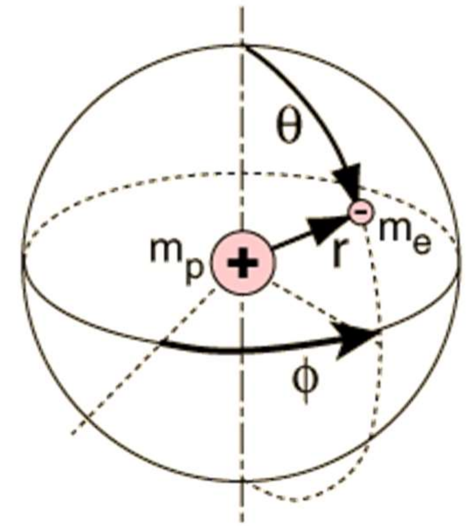
$$= E_e \cdot \psi_e(x,y,z)$$

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

Spherical Polar Co-ordinates



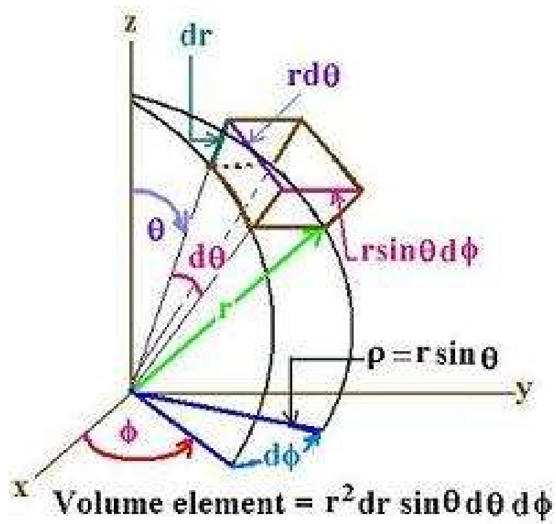
$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$



‘r’ ranges from 0 to ∞

‘θ’ ranges from 0 to π

‘ϕ’ ranges from 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

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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

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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

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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

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

Laplacian in Spherical Coordinates

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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

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

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

Laplacian in Spherical Coordinates

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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

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

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and, for the y-equation:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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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)

$$\begin{aligned}\frac{\partial}{\partial\theta}\Bigg(&+\frac{\cos\theta\sin\theta}{r^2}+\frac{\sin\theta\cos\theta}{r^2}-\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}-\frac{\sin\theta\cos\theta\sin^2\phi}{r^2}+\frac{\cos^2\phi\cos\theta}{r^2\sin\theta}\\&-\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}-\frac{\sin\theta\cos\theta\cos^2\phi}{r^2}+\frac{\cos\theta\sin^2\phi}{r^2\sin\theta}\Bigg)\\&\rightarrow\frac{\cos\theta}{r^2\sin\theta}\frac{\partial}{\partial\theta}\end{aligned}\tag{75}$$

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

$$\begin{aligned}\frac{\partial}{\partial\phi}\Bigg(&-\frac{\sin\phi\cos\phi}{r^2}-\frac{\cos^2\theta\cos\phi\sin\phi}{r\sin^2\theta}-\frac{\cos^2\theta\cos\phi\sin\phi}{r\sin^2\theta}+\frac{\cos\phi\sin\phi}{r^2}+\left(\frac{\cos\theta\cos\phi}{r}\right)\\&+\left(\frac{\cos\theta\cos^2\phi\sin\phi}{r^2\sin\theta}\right)+\frac{\sin\phi\cos\phi}{r\sin^2\theta}\Bigg)\rightarrow 0\end{aligned}\tag{78}$$

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From Equations 57 and 74 we obtain

$$\frac{\partial^2}{\partial\phi^2}\left(\frac{\cos^2\phi}{r^2\sin^2\theta}+\frac{\sin^2\phi}{r^2\sin^2\theta}\right)\rightarrow\left(\frac{1}{r^2\sin^2\theta}\right)\frac{\partial^2}{\partial\phi^2} \tag{79}$$

The mixed derivatives yield, first, from Equations 45, 53, 62, and 70 leading to

$$\frac{\partial^2}{\partial r\partial\phi}\left(\frac{\cos\phi\sin\phi}{r}+\frac{\cos\phi\sin\phi}{r}-\frac{\sin\phi\cos\phi}{r}-\frac{\sin\phi\cos\phi}{r}\right)\rightarrow 0 \tag{80}$$

From Equations 36, 39, 47, 43 64, 60

$$\begin{aligned}&\frac{\partial^2}{\partial r\partial\theta}\left(-\frac{\sin\theta\cos\theta}{r}-\frac{\sin\theta\cos\theta}{r}+\frac{\cos\theta\sin\theta\sin^2\phi}{r}\right.\\&\left.+\frac{\sin\theta\cos\theta\cos^2\phi}{r}+\frac{\cos\theta\sin\theta\sin^2\phi}{r}+\frac{\sin\theta\cos\theta\cos^2\phi}{r}\right)\rightarrow 0\end{aligned} \tag{81}$$

From Equations 51 55 68 72

$$\begin{aligned}&\frac{\partial^2}{\partial\phi\partial\theta}\left(\frac{\cos\theta\cos\phi\sin\phi}{r^2\sin\theta}+\frac{\cos\phi\sin\phi}{r^2\sin\theta}\right.\\&\left.-\left(\frac{\sin\phi\cos\phi\cos\theta}{r^2\sin\theta}\right)-\left(\frac{\cos\theta\sin\phi\cos\phi}{r^2\sin\theta}\right)\right)\rightarrow 0\end{aligned} \tag{82}$$

Gathering together the non-vanishing terms, we obtain

$$\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}+\frac{\cos\theta}{r^2\sin\theta}\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

which is one of the two "classic" forms for ∇^2. The other is

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

Spherical Polar Co-ordinates

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)f$$

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

$$\psi_e \Rightarrow \psi_e(r,\theta,\phi) \Leftarrow \psi_e(x,y,z)$$

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

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

Separation of variables

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

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

Multiply with $\frac{-2\mu r^2}{\hbar^2}$

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

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

Separation of variables

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

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

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

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

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

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

Separation of variables

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

Rearrange

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

Separation of variables

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

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

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

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

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

Rearrange

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

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

LHS = $f(r)$=$f(\theta,\phi)$ =RHS

$\Rightarrow f(r)$=$f(\theta,\phi)$ =constant=β

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

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

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

LHS = $f(r)$=$f(\theta,\phi)$ =RHS

$\Rightarrow f(r)$=$f(\theta,\phi)$ =constant=β

Separation of variables

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

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

Let us consider

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

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

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

Separation of variables

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

$$\boxed{\begin{array}{l}\text{LHS} = f(\theta)=f(\phi) = \text{RHS} \\ \Rightarrow f(\theta)=f(\phi) = \text{constant} = m^2\end{array}}$$

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

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

Separation of variables

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

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

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

We have separated out all the three variables r, θ and ϕ

Solution to Φ part

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

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

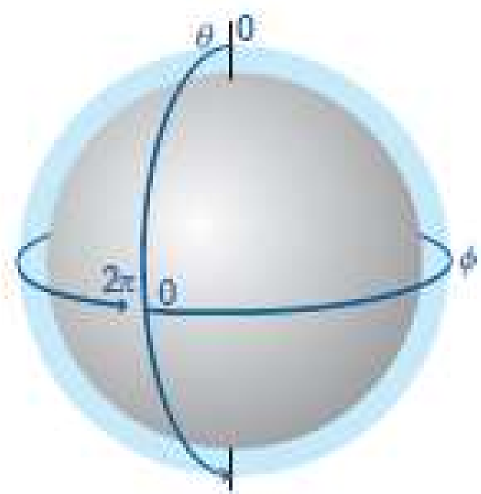
Let is assume

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

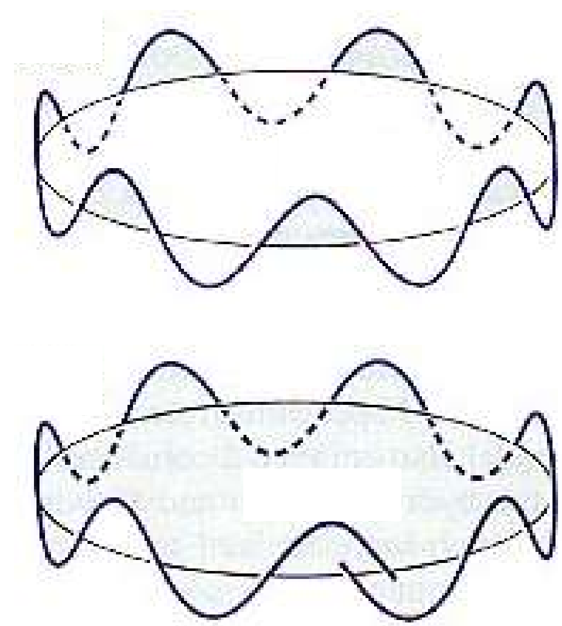
as trial solution

$$\frac{\partial\Phi}{\partial\phi}=\pm im\Phi 0$$

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



‘ϕ’ ranges from 0 to 2π



Wavefunction has to be continuous

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

Solution to Φ part

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

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

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

True only if 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 $|m|<l$

The Θ and the R part

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

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

Rearrange

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

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

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 $\Theta(\theta)$

Restriction on m are due this this equation

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 $\Theta(\theta)$ are

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

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

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

l=0,1,2,3…

$P_l^m(\cos\theta)$ are known as Associated Legendre Polynomials

The new quantum number is 'l' called orbital / Azimuthal quantum number

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

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

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

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

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

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

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

Orbital Angular Momentum Quantum Number

l=0 $\Rightarrow$ *s*-Orbital

l=1 $\Rightarrow$ *p*-Orbital

l=2 $\Rightarrow$ *d*-Orbital

l=3 $\Rightarrow$ *f*-Orbital

Normalization

$$\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)\cdot Y_l^m(\theta,\phi)$$

$$\Rightarrow$$

$$\left|\psi_{n,l,m}(r,\theta,\phi)\right|^2 = \left|R_{n,l}(r)\cdot Y_l^m(\theta,\phi)\right|^2 = \left|R_{n,l}(r)\right|^2\cdot\left|Y_l^m(\theta,\phi)\right|^2$$

Normalize the Radial and Angular parts separately

$$\int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left|\psi_{n,l,m}(r,\theta,\phi)\right|^2 = 1$$

$$\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left|Y_l^m(\theta,\phi)\right|^2 = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \left[Y_l^m(\theta,\phi)\right]^* Y_l^m(\theta,\phi) = 1$$

$$\int_0^\infty r^2 dr \left|R_{n,l}(r)\right|^2 = \int_0^\infty dr \left[R_{n,l}(r)\right]^* R_{n,l}(r) = 1$$

Spherical Harmonics Y_l^m

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

$$l=0; m=0 \quad \left(\frac{1}{4\pi}\right)^{1/2}$$

$$l=1; m=0 \quad \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$l=1; m=\pm1 \quad \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

$$l=2; m=0 \quad \left(\frac{3}{8\pi}\right)^{1/2} \left(3\cos^2\theta-1\right)$$

$$l=2; m=\pm1 \quad \mp\left(\frac{15}{8\pi}\right)^{1/2} \cos\theta\sin\theta e^{\pm i\phi}$$

$$l=2; m=\pm2 \quad \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

$$l=3; m=0 \quad \left(\frac{7}{16\pi}\right)^{1/2} \left(5\cos^3\theta-3\cos\theta\right)$$

$$l=3; m=\pm1 \quad \mp\left(\frac{21}{64\pi}\right)^{1/2} \left(5\cos^2\theta-1\right)\sin\theta e^{\pm i\phi}$$

$$l=3; m=\pm2 \quad \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$$

$$l=3; m=\pm3 \quad \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$$

Radial Functions

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

$$n=1; l=0 \quad 2\left(\frac{Z}{a}\right)^{3/2} e^{-\rho/2}$$

$$n=2; l=0 \quad \frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (2-\rho) e^{-\rho/2}$$

$$n=2; l=1 \quad \frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho e^{-\rho/2}$$

$$n=3; l=0 \quad \frac{1}{243^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \left(6-6\rho-\rho^2\right) e^{-\rho/2}$$

$$n=3; l=1 \quad \frac{1}{486^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (4-\rho) e^{-\rho/2}$$

$$n=3; l=2 \quad \frac{1}{2430^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho^2 e^{-\rho/2}$$

$$\rho = \frac{2Zr}{na}$$

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

$$a = a_0 \quad (\text{for } \mu = m_e)$$

Radial Functions of Hydrogen Atom

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

$$n=1; l=0 \quad 2\left(\frac{1}{a_o}\right)^{3/2} e^{-r/a_o}$$

$$n=2; l=0 \quad \frac{1}{8^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}$$

$$n=2; l=1 \quad \frac{1}{24^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{r}{a_o}\right)e^{-r/2a_o}$$

$$n=3; l=0 \quad 2\left(\frac{1}{3a_o}\right)^{3/2}\left(1-\frac{2}{3}\left[\frac{r}{a_o}\right]-\frac{2}{27}\left[\frac{r}{a_o}\right]^2\right)e^{-r/3a_o}$$

$$n=3; l=1 \quad \frac{1}{486^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(4-\frac{2r}{3a_o}\right)e^{-r/3a_o}$$

$$n=3; l=2 \quad \frac{1}{2430^{1/2}}\left(\frac{1}{a_o}\right)^{3/2}\left(\frac{2r}{3a_o}\right)^2 e^{-r/3a_o}$$

$$\rho = \frac{2Zr}{na}$$

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

$$a = a_o \quad (\text{for } \mu = m_e)$$

Wavefunctions of Hydrogen Atom

$$\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)\cdot Y_l^m(\theta,\phi)$$

$$\psi_{1,0,0} = \psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} \boxed{e^{-r/a_o}} \qquad f(r)$$

$$\psi_{2,0,0} = \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2} \boxed{\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}} \qquad f(r)$$

$$\psi_{2,1,0} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2} \boxed{\left(\frac{r}{a_o}\right)e^{-r/2a_o}}\boxed{\cos\theta} \qquad f(r,\theta)$$

$$\psi_{2,1,+1} = \psi_{2p_{+1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} \boxed{\left(\frac{r}{a_o}\right)e^{-r/2a_o}}\boxed{\sin\theta}\boxed{e^{i\phi}} \qquad f(r,\theta,\phi)$$

$$\psi_{2,1,-1} = \psi_{2p_{-1}} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2} \boxed{\left(\frac{r}{a_o}\right)e^{-r/2a_o}}\boxed{\sin\theta}\boxed{e^{-i\phi}} \qquad f(r,\theta,\phi)$$