4E : The Quantum Universe

Lecture 23, May 11

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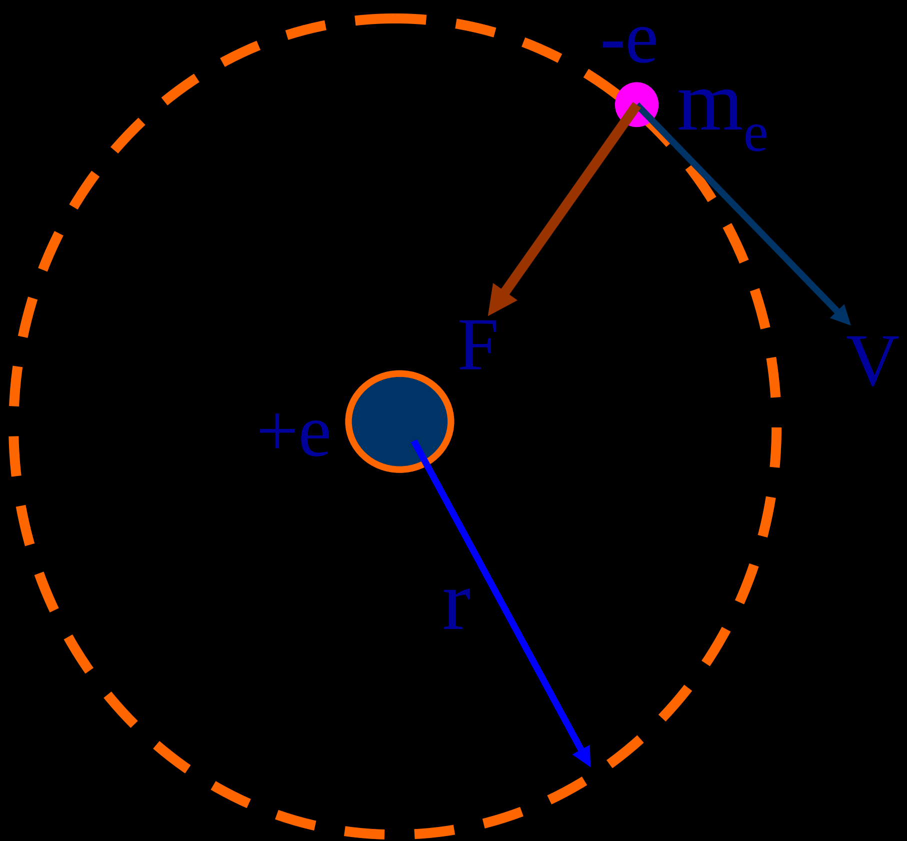
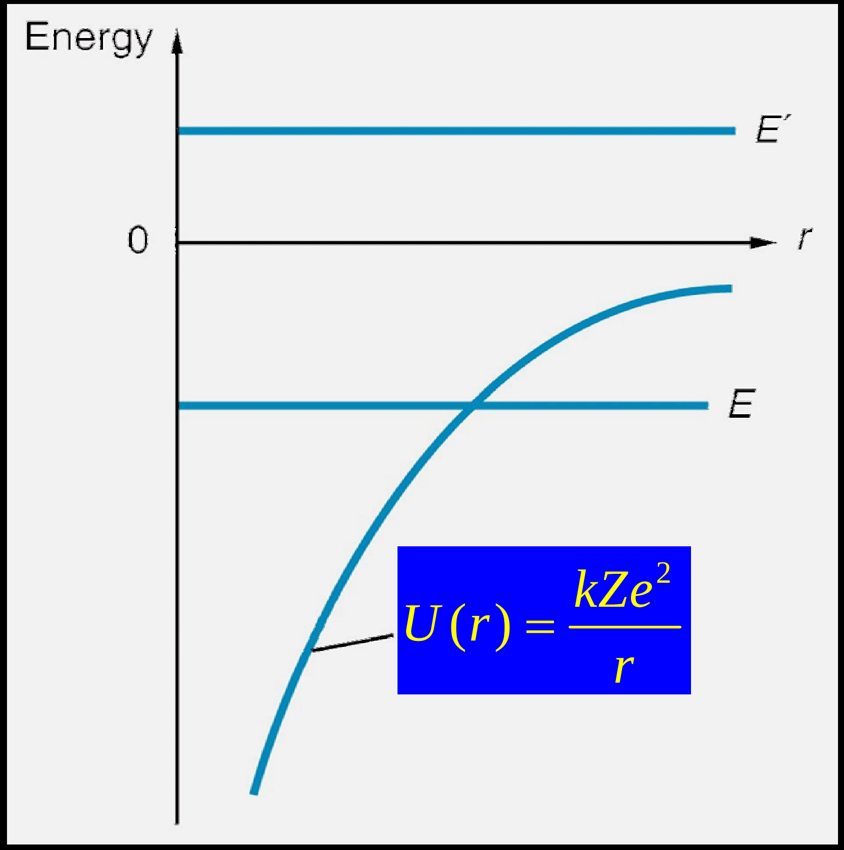
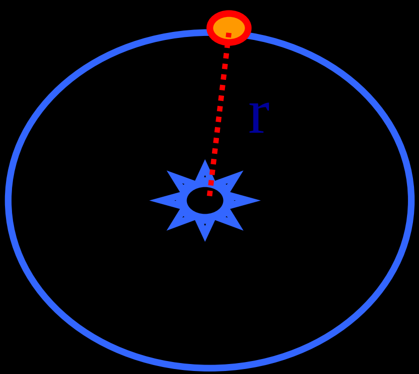
The Coulomb Attractive Potential That Binds the electron and Nucleus (charge +Ze) into a Hydrogenic atom







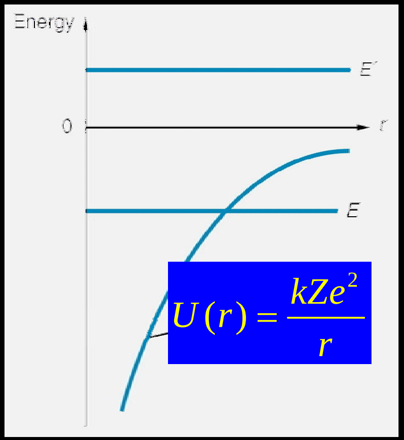
$U(r) \propto \frac{1}{r} = \frac{1}{\sqrt{x^2 + y^2 + z^2}} \Rightarrow$ x,y,z all mixed up !

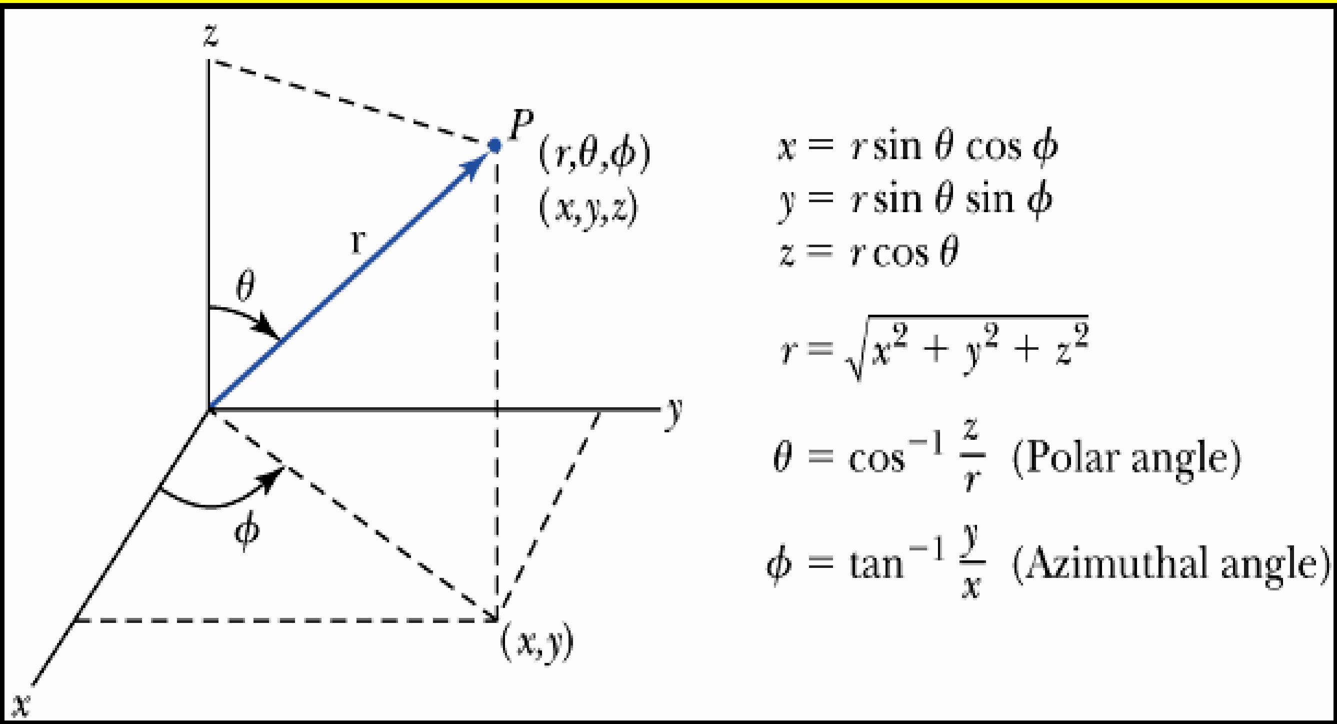
As in case of particle in 3D box, we should use seperation of variables (x,y,z ??) to derive 3 independent differential. eqns.

This approach will get very ugly since we have a "conjoined triplet"

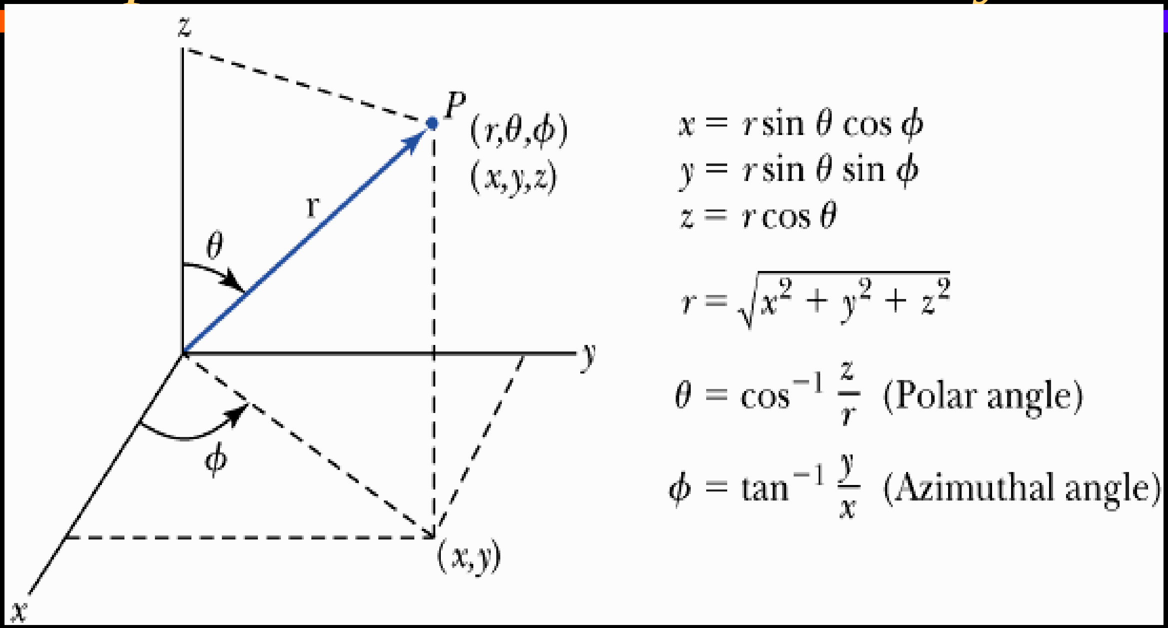
To simplify the situation, choose more appropriate variables

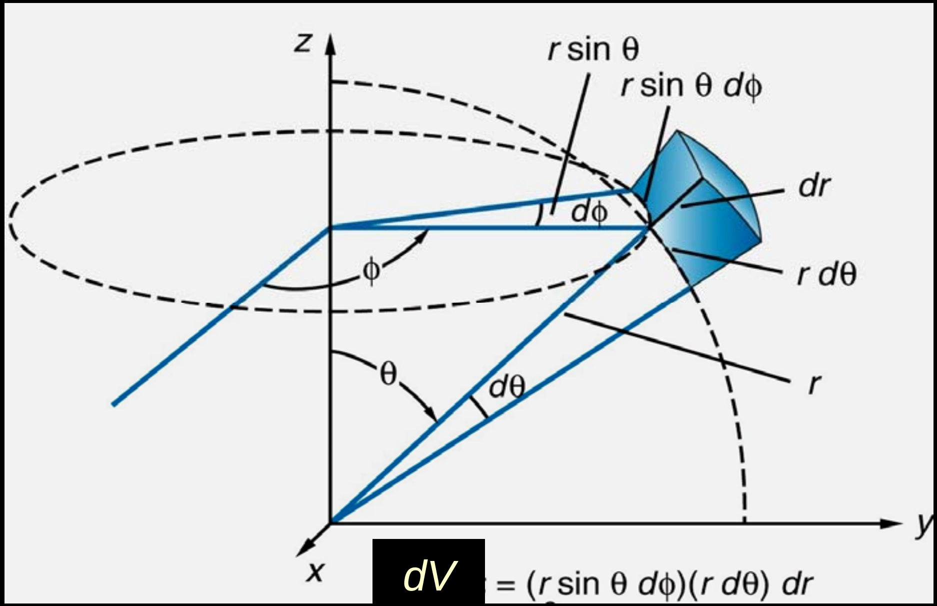
Cartesian coordinates (x,y,z) $\rightarrow$ Spherical Polar (r,θ,ϕ) coordinates





Spherical Polar Coordinate System

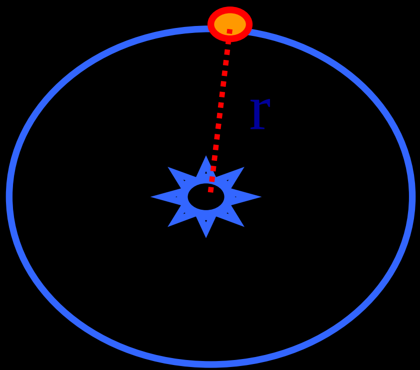


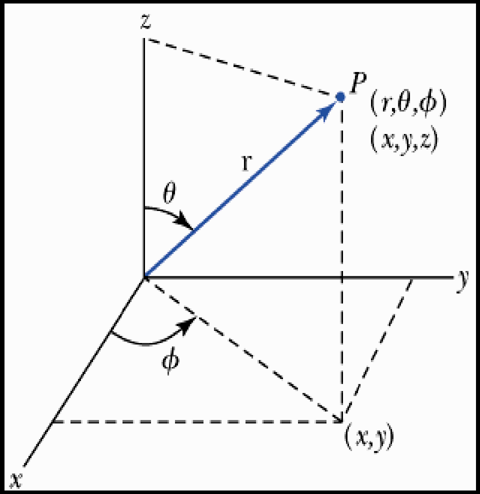


Volume Element dV

$$dV = (r\sin\theta d\phi)(rd\theta)(dr)$$
$$= r^2 \sin\theta dr d\theta d\phi$$

The Hydrogen Atom In Its Full Quantum Mechanical Glory





Instead of writing Laplacian $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$,

write ∇^2 for spherical polar coordinates:

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

Thus the T.I.S.Eq. for $\psi(x,y,z) = \psi(r,\theta,\phi)$ becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right) +$$
$$\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial^2\phi} + \frac{2m}{\hbar^2}(E-U(r))\psi(r,\theta,\phi) = 0$$

with $U(r) \propto \frac{1}{r} = \frac{1}{\sqrt{x^2+y^2+z^2}}$

The Schrodinger Equation in Spherical Polar Coordinates *(is bit of a mess!)*

The TISE is :

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial^2\phi}+\frac{2m}{\hbar^2}(E-U(r))\psi(r,\theta,\phi)=0$$

Try to free up second last term from all except ϕ

This requires multiplying thruout by $\boxed{r^2\sin^2\theta}\Rightarrow$

$$\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{\partial^2\psi}{\partial^2\phi}+\frac{2mr^2\sin^2\theta}{\hbar^2}(E+\frac{ke^2}{r})\psi=0$$

For Seperation of Variables, Write $\psi(r,\theta,\phi) = R(r) . \Theta(\theta) . \Phi(\phi)$

Plug it into the TISE above & divide thruout by $\psi(r,\theta,\phi)=R(r).\Theta(\theta).\Phi(\phi)$

Note that :

$$\boxed{\begin{array}{l}\dfrac{\partial\Psi(r,\theta,\phi)}{\partial r}=\Theta(\theta).\Phi(\phi)\ \dfrac{\partial R(r)}{\partial r}\\ \dfrac{\partial\Psi(r,\theta,\phi)}{\partial\theta}=R(r)\Phi(\phi)\ \dfrac{\partial\Theta(\theta)}{\partial\theta}\\ \dfrac{\partial\Psi(r,\theta,\phi)}{\partial\theta}=R(r)\Theta(\theta)\ \dfrac{\partial\Phi(\phi)}{\partial\phi}\end{array}}\Rightarrow$$

when substituted in TISE

Solving For the Hydrogen Atom: Separation of Variables

Don't Panic: Its simpler than you think !

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

Rearrange by taking the ϕ term on RHS

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2mr^2\sin^2\theta}{\hbar^2}(E+\frac{ke^2}{r})=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial^2\phi}$$

LHS is fn. of r, θ & RHS is fn of ϕ only , for equality to be true for all r, θ, ϕ

$\Rightarrow$ LHS= constant = RHS = m_l^2

Deconstructing The Schrodinger Equation for Hydrogen

Now go break up LHS to seperate the r & θ terms.....

$$\text{LHS:}\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{2mr^2\sin^2\theta}{\hbar^2}(E+\frac{ke^2}{r})=m_l^2$$

Divide Thruout by $\sin^2\theta$ and arrange all terms with r away from $\theta \Rightarrow$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}(E+\frac{ke^2}{r})=\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$$

Same argument : LHS is fn of r, RHS is fn of θ;

For them to be equal for all r,$\theta \Rightarrow$ $\boxed{\text{LHS = const = RHS} = l(l+1)}$

What is the mysterious $l(l+1)$? Just a number like 2(2+1)

So What do we have after all the shuffling!

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

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta(\theta) = 0\ldots\ldots(2)$$

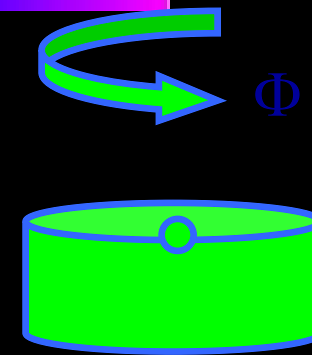
$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right) + \left[\frac{2mr^2}{\hbar^2}(E+\frac{ke^2}{r}) - \frac{l(l+1)}{r^2}\right]R(r) = 0\ldots(3)$$

These 3 "simple" diff. eqn describe the physics of the Hydrogen atom.

All we need to do now is guess the solutions of the diff. equations

Each of them, clearly, has a different functional form

And Now the Solutions of The S. Eqns for Hydrogen Atom



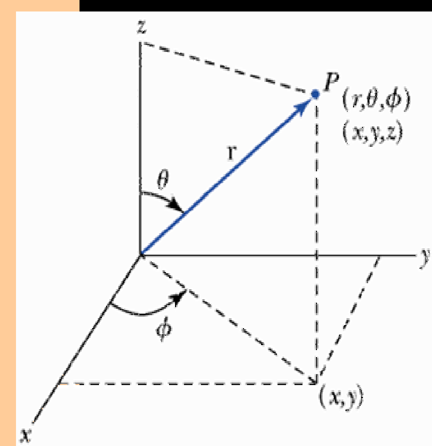
The Azimuthal Diff. Equation : $\boxed{\dfrac{d^2\Phi}{d\phi^2} + m_l^2 \Phi = 0}$

Solution : $\Phi(\phi) = A\, e^{im_l\phi}$ but need to check "Good Wavefunction Condition"

Wave Function must be Single Valued for all $\phi \Rightarrow \Phi(\phi) = \Phi(\phi + 2\pi)$

$\Rightarrow \Phi(\phi) = A\, e^{im_l\phi} = A\, e^{im_l(\phi+2\pi)} \Rightarrow m_l = 0, \pm1, \pm2, \pm3....$(*Magnetic* Quantum #)

The Polar Diff. Eq: $\boxed{\dfrac{1}{\sin\theta}\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right) + \left[l(l+1) - \dfrac{m_l^2}{\sin^2\theta}\right]\Theta(\theta) = 0}$



Solutions : go by the name of "Associated Legendre Functions"

only exist when the integers l and m_l are related as follows

$m_l = 0, \pm1, \pm2, \pm3.... \pm l$; l = positive number

l : Orbital Quantum Number