PHYS-3301

Lecture 16

Oct. 17, 2024

Chapter. 7
QM in 3-dims & Hydrogen Atom

Outline:

- The Schrödinger Eq. in 3-Dimensions
- The 3D Infinite Well
- Energy Quantization & Spectral Lines in Hydrogen
- The Schrödinger Eq. for a Central Force
- Angular Behavior in a Central Force
- The Hydrogen Atom
- Radial Probability
- Hydrogen-like Atoms

Stationary States in a 3-D Box

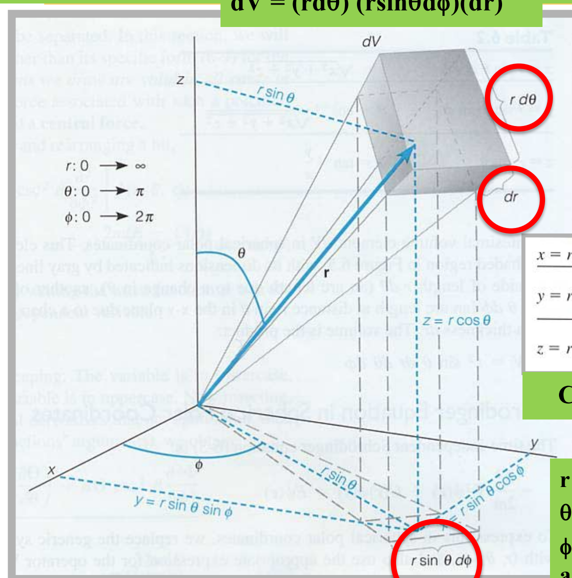
Solution

$$\psi_{n_x,n_y,n_z}(x,\ y,\ z) = A \sin\frac{n_x \pi x}{L_x} \sin\frac{n_y \pi y}{L_y} \sin\frac{n_z \pi z}{L_z}$$

$$E_{n_x,n_y,n_z} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)\frac{\pi^2\hbar^2}{2m}$$

To calculate Prob., (e.g., normalization integral), we need the expression for the infinitesimal Volume element dV in spherical polar coordinator.

dV = (rdθ) (rsinθdϕ)(dr)



Spherical Polar Coordinate system

Best choice

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

Cartesian-polar conversions

r = radius
θ = polar angle b/w r and z-axis
ϕ = azimuthal angle b/w x-axis and projection of r in x-y planes

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}, t) + U(\mathbf{r})\Psi(\mathbf{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t)$$

Schrodinger equation in Spherical Polar Coordinates

See geometry text book

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

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \csc^2\theta\frac{\partial^2}{\partial\phi^2}\right]\psi(r, \theta, \phi) + U(r, \theta, \phi)\psi(r, \theta, \phi) = E\psi(r, \theta, \phi) \quad \text{(6-10)}$$

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

Toward the Hydrogen Atom

To understand what this tell us, we break it into pieces.

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

i.e. separation variables for a central force (see p247)

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

After canceling, we find that one of the variables is separate.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\Theta}\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \csc^2\theta\left[\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}\right] = -r^2\frac{2m(E - U(r))}{\hbar^2} \quad \text{(6-11)}$$

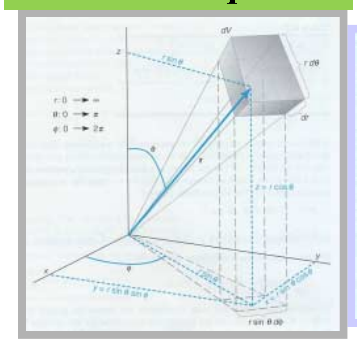
ϕ—separate

7.5 Angular Behavior in a Central Force

$$\frac{d^2\Phi(\phi)}{d\phi^2} = C_\phi\Phi(\phi) \qquad C_\phi = -m_\ell^2$$

Azimuthal Equation

Must be oscillatory



$$\frac{d^2\Phi(\phi)}{d\phi^2} = -m_\ell^2\Phi(\phi)$$

with general solution

$$\Phi(\phi) = Ae^{+im_\ell\phi} + Be^{-im_\ell\phi}$$

$$\Phi_{m_\ell}(\phi) = e^{im_\ell\phi} \quad (m_\ell = 0, \pm1, \pm2, \pm3, \ldots)$$

m_l = Magnetic Quantum number

** Circle's circumference would be an integral number of wavelength:

$2\pi r = m_l\lambda = m_l(h/p) = m_l(h/mv_t) = m_lh/mv_t$

→ $m_l\hbar = mv_tr$

$= r \times p = L_z$

Standing waves on the ϕ-axis

[see Fig. 7-9]

Introduce an "angular momentum operator"!!

Toward the Hydrogen Atom

Quantization of Angular Momentum

$$\hat{L}_z = -i\hbar(\partial/\partial\phi).$$

Angular momentum operator

$$\hat{L}_z^2\Phi_{m_\ell}(\phi) = (m_\ell\hbar)^2\Phi_{m_\ell}(\phi)$$

$$\Phi_{m_\ell}(\phi) = e^{im_\ell\phi} \quad (m_\ell = 0, \pm1, \pm2, \pm3, \ldots)$$

Angular Momentum Operator?

**** Check this out if it works or not!! ****

$$\hat{L}_z = -i\hbar(\partial/\partial\phi).$$

$$\begin{aligned}
-i\hbar\frac{\partial}{\partial\phi} &= -i\hbar\left(\frac{\partial x}{\partial\phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\phi}\frac{\partial}{\partial y} + \frac{\partial z}{\partial\phi}\frac{\partial}{\partial z}\right)\\
&= -i\hbar\left(-r\sin\theta\sin\phi\frac{\partial}{\partial x} + r\sin\theta\cos\phi\frac{\partial}{\partial y} + 0\frac{\partial}{\partial z}\right)\\
&= -i\hbar\left(-y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}\right)\\
&= -y\left(-i\hbar\frac{\partial}{\partial x}\right) + x\left(-i\hbar\frac{\partial}{\partial y}\right)\\
&= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x
\end{aligned}$$

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

YES

r x p = L_z

Angular Momentum Operator

$$\hat{L}_z^2\Phi_{m_\ell}(\phi) = (m_\ell\hbar)^2\Phi_{m_\ell}(\phi)$$

$$L_z = m_\ell\hbar \quad (m_\ell = 0, \pm1, \pm2, \pm3, \ldots)$$

Toward the Hydrogen Atom

We break it into pieces.

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

i.e. separation variables for a central force (see p247)

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

After canceling, we find that one of the variables is separate:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\Theta}\csc\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \csc^2\theta\left[\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}\right] = -r^2\frac{2m(E-U(r))}{\hbar^2} \quad (6\text{-}11)$$

ϕ—separate

$-m_l^2$