Physics 492

Lecture 2

$$\hat{H}_H = \frac{1}{2\mu}|\hat{\vec{p}}|^2 + V(\hat{r})$$ hydrogen atom

where $\hat{\vec{r}}, \hat{\vec{p}}$ are relative coordinates

$$\hat{H}|E\rangle = E|E\rangle$$ energy eigenstates

states $|E\rangle$ are labeled by additional "good" quantum number which are eigenvalues of Complete set of commuting observables (CSCO)

$$[\hat{H}, \hat{O}_i] = 0 \quad [\hat{O}_i, \hat{O}_j] = 0$$

where complete means no more such operators exist. Completeness depends on degrees of freedom we consider for the system. For now we ignore spin.

example: free particle

$$\hat{H}|\vec{p}\rangle = \frac{p^2}{2m}|\vec{p}\rangle \quad [\hat{H}, \hat{p}_i] = 0, \; [p_i, p_j] = 0$$

states $|p,0,0\rangle, |0,p,0\rangle, |0,0,p\rangle$ are degenerate

$$\langle \vec{r}|\vec{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} \exp\left(\frac{i\,\vec{r}\cdot\vec{p}}{\hbar}\right)$$

plane waves

For spatial wave function,

$$\langle \vec{r} | \psi \rangle = \psi(\vec{r})$$

eigenstate of $\hat{H}_H$ should be rotationally invariant.

$$[\hat{H}, \hat{L}^2] = 0$$

$$[\hat{H}, \hat{L}_z] = 0$$

$$[\hat{L}^2, \hat{L}_z] = 0$$

CSCO

E, l, m are "good" Q.N.

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

CSCO =
Complete Set of Commutating Observables

energy eigenstate $|E, l, m\rangle$

In position space, $\vec{L} \xrightarrow[r]{} \vec{r} \times \left(\frac{\hbar}{i} \vec{\nabla}\right)$

We can easily show that $\hat{L}_i$ are generators of rotation and that they are components of a vector operator.

$$\hat{R}(\vec{\theta}) = \exp\left(-i \vec{\theta} \cdot \hat{\vec{L}} / \hbar\right)$$

Let $|\psi'\rangle = \hat{R}(\varepsilon \hat{z}) |\psi\rangle = \left(1 - i\varepsilon \hat{L}_z / \hbar\right) |\psi\rangle$

$$\langle \vec{r}|\psi'\rangle = \langle \vec{r}|\hat{R}(\varepsilon\hat{z})|\psi\rangle$$

$$|r'\rangle = \hat{R}(-\varepsilon\hat{z})|r\rangle = |x+\varepsilon y, -\varepsilon x+y, z\rangle$$

thus

$$\langle \vec{r}|\psi'\rangle = \langle \vec{r}|(1 - i\varepsilon \hat{L}_z/\hbar|\psi\rangle$$

$$= \langle x+\varepsilon y, -\varepsilon x+y, z|\psi\rangle$$

$$= \psi(x+\varepsilon y, -\varepsilon x+y, z)$$

$$= \psi(\vec{r}) + \varepsilon y\frac{\partial\psi}{\partial x} - \varepsilon x\frac{\partial\psi}{\partial y}$$

$$\langle \vec{r}|\hat{L}_z|\psi\rangle = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi$$

thus $\hat{L}_z \xrightarrow[r]{} \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \frac{\hbar}{i}(\vec{r}\times\vec{\nabla})_z$

Our definition of $\hat{\vec{L}}$ from classical $\vec{L}$ is justified.

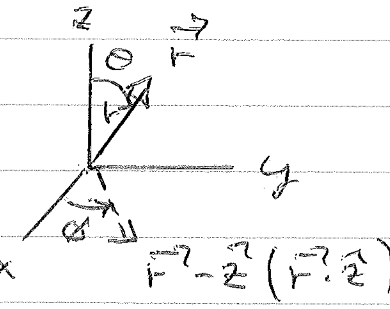
Spherical coordinates and separation of variables

$$\langle \vec{r}\,|\psi\rangle = \psi(r,\theta,\phi)$$

$\theta \equiv$ polar coordinate

$\phi \equiv$ azimuthal coordinate

$r \equiv$ radial coordinate



$$\vec{r} = (r\cos\phi\,\hat{x} + r\sin\phi\,\hat{y})\sin\theta + r\cos\theta\,\hat{z}$$

from H.W. identity

$$\hat{L}^2 = (\hat{\vec{r}}\cdot\hat{\vec{r}})(\hat{\vec{p}}\cdot\hat{\vec{p}}) - (\hat{\vec{r}}\cdot\hat{\vec{p}})^2 + i\hbar\,\hat{\vec{r}}\cdot\hat{\vec{p}}$$

$$\hat{L}^2 \xrightarrow[r]{} r^2\left(\frac{\hbar}{i}\right)^2\nabla^2 - \left(\frac{\hbar}{i}\vec{r}\cdot\vec{\nabla}\right)^2 + i\hbar\,\vec{r}\cdot\left(\frac{\hbar}{i}\vec{\nabla}\right)$$

with $\vec{\nabla} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}$

$\hat{r}, \hat{\theta}, \hat{\phi}$ unit vectors not operators

then $\frac{\hbar}{i}\vec{r}\cdot\vec{\nabla} = \frac{\hbar}{i}r\frac{\partial}{\partial r}$

$$-\left(\frac{\hbar}{i}\vec{r}\cdot\vec{\nabla}\right)^2 = +\hbar^2\left(r\frac{\partial}{\partial r}\right)^2 = +\hbar^2\left(r^2\frac{\partial^2}{\partial r^2} + r\frac{\partial}{\partial r}\right)$$

$$i\hbar\,\vec{r}\cdot\left(\frac{\hbar}{i}\vec{\nabla}\right) = \hbar^2 r\frac{\partial}{\partial r}$$

$$\boxed{\hat{L}^2 \xrightarrow[r]{} -\hbar^2 r^2\nabla^2 + \hbar^2\left(r^2\frac{\partial^2}{\partial r^2} + 2r\frac{\partial}{\partial r}\right)}$$

$$\hat{p}^2 \xrightarrow[r]{} -\hbar^2 \nabla^2 = -\hbar^2\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{r^2}$$

$$\hat{H}_H = \frac{\hat{p}^2}{2\mu} + V(\hat{r}) \xrightarrow[r]{}$$

$$\underbrace{-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)}_{\text{radial K.E.}} + V(r) + \underbrace{\frac{\hat{L}^2}{2\mu r^2}}_{\text{rot. K.E.}}$$

rewrite $\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} = \frac{1}{r}\frac{\partial^2}{\partial r^2} r = \left(\frac{1}{r}\frac{\partial}{\partial r} r\right)^2$

interpret $\frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r} r \equiv \hat{P}_r$: radial momentum operator

$$\hat{H}_H = \frac{\hat{P}_r^2}{2\mu} + V(r) + \frac{\hat{L}^2}{2\mu r^2}$$

$\vec{\hat{L}}$ in spherical coordinates does not depend on r:

$$\hat{\vec{L}} \rightarrow \vec{r} \times \frac{\hbar}{i}\vec{\nabla}$$

$$= (r\hat{r}) \times \left(\hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi}\right)$$

1/r factors cancel r factor

$$= \frac{\hbar}{i}\left(\hat{\phi}\frac{\partial}{\partial \theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right)$$

depends only on angular variables

$$\hat{H}_H = \underbrace{\frac{\hat{p}_r^2}{2\mu} + V(r)}_{\hat{H}_{radial}} + \underbrace{\frac{\hat{L}^2}{2\mu r^2}}_{\hat{H}_{rot}}$$

From theory of angular momentum,

spherical harmonics $Y_{\ell m}$

$$\hat{L}^2 Y_{\ell m}(\theta,\phi) = \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta,\phi)$$

$$\hat{L}_z Y_{\ell m}(\theta,\phi) = m\hbar\, Y_{\ell m}(\theta,\phi)$$

where $\ell = 0, 1, 2,$ integer

$-\ell < m < \ell$ m integer

Then

$$\psi_{E_\ell}(r,\theta,\phi) = R_{E_\ell} Y_{\ell m}(\theta,\phi)$$

$\Rightarrow E$ for general $V(r)$ depends on ℓ.

$$\boxed{-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2} r\right) R_{E_\ell}(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} R_{E_\ell}(r) + V(r) R_{E_\ell}(r) = E_\ell R_{E_\ell}(r)}$$

radial equation

We will pause before finding angular wave functions to do some physics.

$\hat{L}_z$ eigenvalue

$$L_z|l,m\rangle = \hbar m|l,m\rangle$$

$$\langle r,\theta,\phi|\hat{L}_z|l,m\rangle = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\underbrace{\langle r,\theta,\phi|l,m\rangle}_{Y_{lm}(\theta,\phi)}$$

$$\frac{\hbar}{i}\frac{\partial}{\partial\phi}Y_{lm}(\theta,\phi) = m\hbar\, Y_{l,m}(\theta,\phi)$$

$$Y_{lm}(\theta,\phi) = e^{im\phi}\,\Theta(\theta)$$ separation of variables

single valued $\quad e^{im\phi} = e^{im(\phi+2\pi)}$

$m = 0, \pm 1, \pm 2$

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

also, $\hat{L}_z$ must be Hermitian (see text)