Lecture $\boxed{27}$, Nov. 2 (Mon.)

— Outline for today (and rest of week)

→ Rotation matrix elements in terms of spherical harmonics

→ Solving Schroedinger's wave equation for spherically symmetric potential: angular part of wavefunction is spherical harmonics, so focus on radial equation (finding spectrum)

→ general features based on form of potential

→ specific examples ...

Spherical harmonics (new viewpoints): "deduced" from angular momentum eigenkets earlier; next, connection to rotation matrices

$\boxed{\text{Big}}$ picture / basic idea & result

– Start with

$$\langle l, m \underbrace{|\hat{n}\rangle}_{\substack{\text{general}\\ \text{direction}\\ \text{eigenket}}} = \langle l, m| \overbrace{\mathcal{D}(R)}^{\text{rotation operator}} \underbrace{|\hat{z}\rangle}_{\substack{\text{unit vector}\\ \text{along } z\text{-axis}}}$$

– Use $\langle \hat{n} | l, m\rangle = Y_l^m(\theta, \phi)$ on LHS ... related to $\underbrace{\langle l, m | \mathcal{D}(R) | l, m' \rangle}_{\text{rotation matrix elements}}$ on RHS ...

– $\boxed{\text{Claim}}$ (see proof after check)

$$\boxed{\mathcal{D}^{(l)}_{m\,0}(\alpha, \beta, \gamma = 0) = \sqrt{\frac{4\pi}{(2l+1)}}\; Y_l^{m*}(\theta, \phi)}$$

row ↗ (m), column ↑ (0)

$\boxed{\text{evaluated at } \theta = \beta,\ \phi = \alpha}$

– cross-check with earlier result :

Review of rotation matrix using Euler angles

$$\mathcal{D}^{(j)}_{m'm}(\alpha,\beta,\gamma) = \langle j,m'|\underbrace{\exp\left(\frac{-iJ_z\alpha}{\hbar}\right)}_{\mathcal{D}_z(\alpha)}\overbrace{\exp\left(\frac{-iJ_y\beta}{\hbar}\right)}^{\mathcal{D}_y(\beta)}\overbrace{\exp\left(\frac{-iJ_z\gamma}{\hbar}\right)}^{\mathcal{D}_z(\gamma)}|j,m\rangle$$

Euler angles

$e^{-im'\alpha}$ $\qquad$ $e^{-im\gamma}$

$$\equiv e^{-i(m'\alpha+m\gamma)}\underbrace{d^{(j)}_{m'm}(\beta)}$$

$$\equiv \langle j,m'|\exp\left(\frac{-iJ_y\beta}{\hbar}\right)|j,m\rangle$$

$$\text{So, } \mathcal{D}^{(\ell)}_{m\,0}(\alpha,\beta,\cancel{0}^{\,\gamma}) = e^{-im\alpha}\, d^{(j)}_{m\,0}\, e^{-i\,0\cdot 0}$$

γ $\qquad$ "other" m

(use above claim) $= \sqrt{\dfrac{4\pi}{(2\ell+1)}}\, Y_\ell^{m*}(\beta,\alpha) \Rightarrow$

$$d^{(\ell)}_{m\,0}(\beta) = \sqrt{\frac{4\pi}{(2\ell+1)}}\,\frac{Y_\ell^{m*}(\beta,\alpha)}{e^{-im\alpha}}$$

no α $\qquad$ ϕ $\qquad$ $\propto P_\ell^m(\cos\theta)$

Recall: $Y_\ell^m(\theta,\phi) = \boxed{e^{-im\phi}}\, f_\ell^m(\theta) \Rightarrow$

$$d^{(\ell)}_{m\,0}(\beta) = \sqrt{\frac{4\pi}{(2\ell+1)}}\, f_\ell^m(\beta)$$

(α-dependence cancels on RHS)

Specifically, $\ell = 1$: use $Y_1^{0,\pm 1}\}\, m$

$$d^{(1)}_{m\,0}(\beta) = \sqrt{\frac{4\pi}{3}} \begin{cases} \sqrt{\dfrac{3}{4\pi}}\cos\beta & m=0 \\ \mp\sqrt{\dfrac{3}{8\pi}}\sin\beta & m=\pm 1 \end{cases}$$

column index

$$= \begin{cases} \cos\beta & m=0 \\ \mp \sin\beta/\sqrt{2} & m=\pm 1 \end{cases}$$

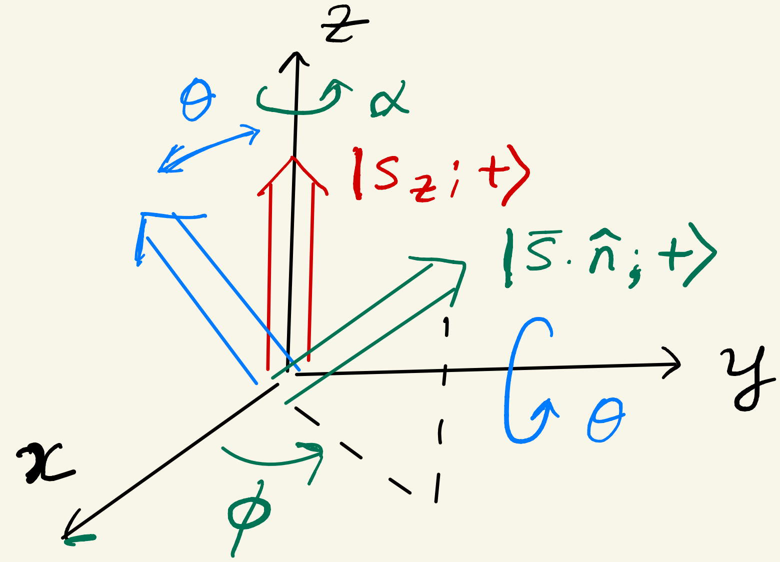
... agrees with middle column of Eq. 3.5.57 of Sakurai / slide 8 of lecture 25 on Oct. 28

$\boxed{\text{Proof}}$ of claim: recall rotating from $|S_z;+\rangle$ to $|\bar{S}\cdot\hat{n};+\rangle$ using

$$\mathcal{D}(\alpha = \phi,\ \beta = \theta,\ \gamma = 0)$$

rotate about z-axis by ϕ

1st rotate about y-axis



$\Longrightarrow$

$$\underbrace{\langle l,m|\hat n\rangle}_{Y_l^m(\theta,\phi)} = \sum_{m'} \underbrace{\langle l,m|\mathcal{D}(R)|l,m'\rangle}_{\mathcal{D}^{(l)}_{mm'}}\langle l,m'|\hat z\rangle \quad \cdots(1)$$

(Again $|l,m\rangle$ for fixed l, but varying m form complete set)

→ $\boxed{\text{Work on}}$ $\langle l,m'|\hat z\rangle$ for "collapsing" $\boxed{\sum_{m'}}$

– Using $Y_l^m(\hat n) = \langle \hat n|l,m\rangle$; we get

$$\langle l,m|\hat z\rangle = Y_l^m(\theta,\phi)\Big|_{\substack{\theta=0\\ \text{any }\phi}} \quad \cdots(2)$$

– (Mini) claim: $\langle l,m|\hat z\rangle = 0$ if $m\neq 0$

because $L_z|\hat z\rangle = (xp_y - yp_x)|\hat z\rangle$
$= 0$

so that $\langle l, m | \underbrace{L_z}_{m} | \hat{z} \rangle$ $\quad \hat{z} \to 0$

$= m \langle l, m | \hat{z} \rangle = 0$, i.e.,

$m \neq 0 \Rightarrow \langle l, m | \hat{z} \rangle = 0 \quad \ldots (3)$

Combining (2) & (3) gives

$\langle l, m | \hat{z} \rangle = \delta_{m0} Y_l^{m*}(\theta = 0, \phi \text{ not fixed})$ $\leftarrow$ set to 0

$= \underbrace{\delta_{m0} \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta)}_{Y_l^0} \Big|_{\cos\theta = 1}$

$P_l(1) = 1$

$\Rightarrow \langle l, m | \hat{z} \rangle = \sqrt{\frac{2l+1}{4\pi}} \, \delta_{m0} \quad \ldots (4)$

Plug (4) into RHS of (1) gives

$Y_l^m(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} \left(\text{"no"} \sum_{m'} \right) \mathcal{D}^{(l)}_{m0}(\underset{\alpha}{\phi}, \underset{\beta}{\theta}, \underset{\gamma}{0})$

i.e., $\mathcal{D}^{(\ell)}_{m0}(\alpha,\beta,\gamma=0) = \sqrt{\frac{4\pi}{2\ell+1}}\, Y_\ell^{m*}(\theta,\phi)$

$\theta = \beta, \quad \phi = \alpha$

Special case: $m = 0$

$$\underbrace{d^{(\ell)}_{00}}_{\text{middle row \& column}}(\beta)\Big|_{\beta=\theta} = \underbrace{P_\ell(\cos\theta)}_{}$$

from $Y_\ell^0 = \sqrt{\frac{2\ell+1}{4\pi}}\, P_\ell(\cos\theta)$

Schroedinger's equation for spherically symmetric potential (central force): $V(r)$, $r = |\bar{x}|$

e.g., one-electron atom; 3D isotropic SHO

$\Rightarrow H = |\bar{p}|^2/(2m) + V(r)$

— $\boxed{\text{Classically}}$, $\bar{L}$ (orbital angular momentum) is conserved [no dependence on θ, ϕ (cyclic): $\bar{L}$ conjugate to θ, ϕ]

— Onto QM: schematically/acting on wavefunctions:

$\bar{L} \propto$ "angular" derivatives $\Rightarrow$

$$[\bar{L}, V(r \text{ only})] = 0$$

and $|\bar{p}|^2$ "=" $-\hbar^2 \nabla^2$

$$= \text{radial derivatives} + \frac{|\bar{L}|^2}{2mr^2}$$

so that (using $[\bar{L}, |\bar{L}|^2] = \ )$

$[\bar{L}, |\bar{p}|^2] = 0 \quad \Rightarrow [\bar{L}, H] = 0$

L_x, L_y, L_z separately $\quad = [|\bar{L}|^2, H]$

i.e., similar to $\boxed{\text{classical}}$:

$\boxed{\text{expectation}}$ value of $\boxed{\bar{L}}$ is <u>constant</u> in time ($\boxed{\text{Ehrenfest}}$ theorem)

$\Rightarrow$ Energy eigenstates labeled by

$\boxed{E, \ell, m}$: $H|E\ell m\rangle = E|E, \ell, m\rangle$;

$|\bar{L}|^2 |E\ell m\rangle = \ell(\ell+1)\hbar^2 |E\ell m\rangle$ &

$L_z |E\ell m\rangle = m\hbar |E\ell m\rangle$

— Onto wavefunction representation:

$$\psi_{E\ell m}(\bar{x}') \equiv \langle x' | E\ell m\rangle = Y_\ell^m(\theta,\phi) R_{E\ell m}^{(r)}$$

see below

(separate variables... or use $\bar{L}$ viewpoint)

plugged into Schroedinger's wave equation:

$$-\frac{\hbar^2}{2m}\Bigg[\frac{\partial^2}{\partial r^2}\underbrace{\langle x'|\alpha\rangle}_{\text{in general}} + \frac{2}{r}\frac{\partial}{\partial r}\langle x'|\alpha\rangle\Bigg]\Bigg\}\text{ radial part of } |\bar{p}|^2$$

$$+ V(r')\langle x'|\alpha\rangle + \frac{\langle x'||\bar{L}|^2|\alpha\rangle}{2mr'^2}$$

$$= E\langle x'|\alpha\rangle$$ ... here, $|\alpha\rangle = |E\ell m\rangle$

gives radial equation ("m disappears")

$$\left[-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r)\right] \times R_{E\ell}(r) = E R_{E\ell}(r)$$

from $|\bar{L}|^2$ part of $|\bar{p}|^2$

$\boxed{\text{Goal}}$ (eigenvalue/function problem):

for what E values, do well-defined (satisfying BC) solutions exist?

– General features (effect of angular momentum term) deduced using $R_{E\ell}(r) = \dfrac{u_{E\ell}(r)}{r}$:

$$-\frac{\hbar^2}{2m}\frac{d^2 u_{E\ell}}{dr^2} + \left[\frac{\ell(\ell+1)}{2mr^2}\hbar^2 + V(r)\right]u_{E\ell}$$

$$= E\, u_{E\ell}$$

– Why is this useful?

(1). Normalization of $u_{E\ell}$ simple ("1 d"):

$$1 = \int \underbrace{r^2 dr}_{\text{radial part of 3d volume element}} |R_{E\ell}(r)|^2 \underbrace{\int d\Omega\, |Y_\ell^m(\theta,\phi)|^2}_{=1}$$

$u_{E\ell}/r$

$$\boxed{= \int dr\, |u_{E\ell}|^2}$$

(2). Defining $V_{eff}(r) = V(r) + \left\{\dfrac{\ell(\ell+1)\hbar^2}{2mr^2}\right.$ angular momentum barrier $\to \infty$ as $r \to 0$

(see later for figure)

[recall classical analysis of central

force/potential (see. 3.3 of Goldstein): $V_{eff}(r)$ gives qualitative features of orbit, e.g., bounded or not]

In QM, $u_{E\ell}$ satisfies Schroedinger's wave equation in "1 d", but with V_{eff}:

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} u_{E\ell} + V_{eff}(r) u_{E\ell} = E u_{E\ell}}$$

e.g., for $\ell \neq 0$, amplitude for locating particle near origin ($r \to 0$) small due to angular momentum barrier [except $\ell = 0$ (s-wave)]

More quantitatively, suppose

$$\lim_{r \to 0} r^2 V(r) = 0 \text{ (e.g.,}$$

Coulomb potential (one-electron atom)

so that:

$[-E + V(r)]$ / (angular momentum barrier) ← "other" terms in DE

note [present even for $V=0$ (free particle)]

$\rightarrow 0$ as $r \rightarrow 0$ ($\ell \neq 0$)

i.e., as $\boxed{r \rightarrow 0}$: $\frac{d^2 u_{E\ell}}{dr^2} = \frac{\ell(\ell+1)}{r^2} u_{E\ell}$

$\Rightarrow u(r) = Br^{-\ell} + Ar^{\ell+1}$ $\boxed{\text{(only for } r \rightarrow 0)}$

$-(Br^{-\ell}) \rightarrow \infty$ $(r \rightarrow 0)$: $\boxed{\text{drop?}}$ But volume element $\rightarrow 0$, so not so clear...

$-$Use $\boxed{\text{probability flux}}$ to argue $B = 0$:

$\bar{j} = \frac{\hbar}{m} \, Im(\psi^* \bar{\nabla} \psi)$, with radial component $j_r = \hat{r}.\bar{j} = \frac{\hbar}{m}\left(\psi^* \frac{\partial}{\partial r} \psi\right)$

$= \hbar/m \; R_{E\ell}(r) \, d/dr \, R_{E\ell}(r)$

(a) $R_{E\ell}(r) \longrightarrow r^{\ell}$ (from A term) gives

$j_r \propto \ell\, r^{2\ell-1}$ so that

$$\oint \bar{j}\cdot d\bar{a} = -\frac{d}{dt}\int_V \rho\, dV \quad \text{from } \bar{\nabla}\cdot\bar{j} = \partial\rho/\partial t$$

gives probability to escape from small sphere centered at $\boxed{\text{origin}}$: $\boxed{\text{sensible}}$

$$4\pi r^2 \times j_r \propto \ell\, r^{2\ell+1} \to 0 \text{ as } r\to 0$$

(b) $R_{E\ell}(r) \to r^{-(\ell+1)}$ (from B term)

gives $j_r \propto (\ell+1)\, r^{-2\ell-3}$ so

that probability to escape...

$$= 4\pi r^2 j_r \propto (\ell+1)\, r^{-2\ell-1}$$

$\to \infty$ (as $r\to 0$): problematic (lose intepretation as probability for $|\psi|^2$)

So, choose $u_{E\ell}(r) \propto r^{\ell+1}$ ... $\Rightarrow$

$R_{E\ell}(r) \to r^{\ell}$ as $r\to 0$

(wavefunction at origin $\boxed{\text{vanishes}}$

due to angular momentum barrier [exception: $\ell = 0$ (s-wave)]