Session 13 ~ 14 Hydrogen Atom

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Goal

1. Schrödinger's equation for the hydrogen atom
   How to derive? How to solve? How to interprete?
2. Quantum numbers and its physical meanings.
3. Transitions of electrons

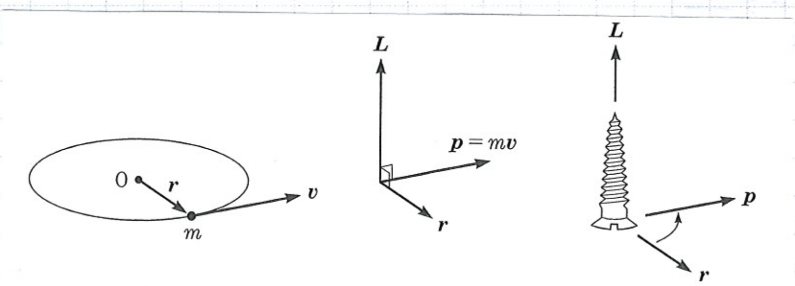
Scenario

✓ Have learned how to describe and solve electron motions
in one dimmension.

✓ In atoms and molecules, electrons rotate around the nuclei.

⇒ Angular momentum

How to deal with the angular momentum in quantum mechanics.



$$L = r \times p$$

$$L = rmv = rp$$

- Angular momentum.

How to describe the angular momentum?

- In one particle system,

$$L = r \times p$$

r: Radius vector.

p: Momentum vector.

$$L = L_x \hat{i} + L_y \hat{j} + L_z \hat{k}$$

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad \text{operator}$$

$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$\hat{L}^2 = \hat{L}\cdot\hat{L} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

- In spherical coordinates,

$$\hat{L}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

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

Commutation relation.

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = i\hbar\hat{L}_z$$

$$[\hat{L}_y, \hat{L}_z] = \hat{L}_y\hat{L}_z - \hat{L}_z\hat{L}_y = i\hbar\hat{L}_x$$

$$[\hat{L}_z, \hat{L}_x] = \hat{L}_z\cdot\hat{L}_x - \hat{L}_x\hat{L}_z = i\hbar\hat{L}_y$$

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

→ Hydrogen atom 3 separated eqs. → Angular part.

- Conversions of partial derivatives from Cartesian to polar coordinates

$$x = r\sin\theta\cos\phi \qquad \frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

$$y = r\sin\theta\sin\phi \qquad \frac{\partial}{\partial y} = \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

$$z = r\cos\theta \qquad \frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}$$

Way of consideration.

$$f(x,y,z) \to f(r,\theta,\phi) \qquad \frac{\partial f}{\partial x}:$$

if $x \to x+\delta x \Rightarrow r \to r+\delta r,\ \theta \to \theta+\delta\theta,\ \phi \to \phi+\delta\phi$

$$df = \frac{\partial f}{\partial r}dr + \frac{\partial f}{\partial\theta}d\theta + \frac{\partial f}{\partial\phi}d\phi$$

$$\Rightarrow \frac{\partial f}{\partial x} = \frac{\partial f}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial f}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial f}{\partial\phi}\frac{\partial\phi}{\partial x}$$

$$\Rightarrow \frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}$$

$$r = \sqrt{x^2+y^2+z^2} \qquad \frac{\partial r}{\partial x} = \frac{1}{2}\frac{2x}{\sqrt{x^2+y^2+z^2}} = \frac{x}{r} = \sin\theta\cos\phi.$$

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

$$\phi = \tan^{-1}\frac{y}{x}$$

☆ $\frac{\partial r}{\partial x} \neq \left(\frac{\partial x}{\partial r}\right)^{-1}$

$\frac{\partial r}{\partial x}$: y, z, fixed

$\frac{\partial x}{\partial r}$: if $r \to r+\delta r$

$\Rightarrow y \to y+\delta y,\ z \to z+\delta z$

$$\frac{\partial}{\partial r} = \frac{\partial x}{\partial r}\frac{\partial}{\partial x} + \frac{\partial y}{\partial r}\frac{\partial}{\partial y} + \frac{\partial z}{\partial r}\frac{\partial}{\partial z}$$

$$\frac{\partial}{\partial \theta} = \frac{\partial x}{\partial \theta}\frac{\partial}{\partial x} + \frac{\partial y}{\partial \theta}\frac{\partial}{\partial y} + \frac{\partial z}{\partial \theta}\frac{\partial}{\partial z}$$

$$\frac{\partial}{\partial \phi} = \frac{\partial x}{\partial \phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi}\frac{\partial}{\partial y} + \frac{\partial z}{\partial \phi}\frac{\partial}{\partial z}$$

$$\frac{\partial}{\partial r} = \sin\theta\cos\phi\frac{\partial}{\partial x} + \sin\theta\sin\phi\frac{\partial}{\partial y} + \cos\theta\frac{\partial}{\partial z}$$

$$\frac{\partial}{\partial \theta} = r\cos\theta\cos\phi\frac{\partial}{\partial x} + r\cos\theta\sin\phi\frac{\partial}{\partial y} - r\sin\theta\frac{\partial}{\partial z}$$

$$\frac{\partial}{\partial \phi} = -r\sin\theta\sin\phi\frac{\partial}{\partial x} + r\sin\theta\cos\phi\frac{\partial}{\partial y}$$

$$\begin{pmatrix} \\ \\ \\ \end{pmatrix} = \begin{pmatrix} & & \\ & & \\ & & \end{pmatrix}\begin{pmatrix} \\ \\ \\ \end{pmatrix}$$

$$\begin{pmatrix} \sin\theta\cos\phi & \frac{\cos\theta\cos\phi}{r} & -\frac{\sin\phi}{r\sin\theta} \\ \sin\theta\sin\phi & \frac{\cos\theta\sin\phi}{r} & \frac{\cos\phi}{r\sin\theta} \\ \cos\theta & -\frac{\sin\theta}{r} & 0 \end{pmatrix}\begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \phi} \end{pmatrix} = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix}$$

- Rigid rotator model

On the spherical plane, $V = 0$

Others $V = \infty$

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$r = \text{const}$, I : Moment of inertia.

$$\Rightarrow \hat{\mathcal{H}} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad ☆$$

Suppose $\theta = \frac{\pi}{2}$. $\Rightarrow$ Rigid rotator in a plane.

$$-\frac{\hbar^2}{2I}\frac{d^2\psi(\phi)}{d\phi^2} = E\psi(\phi)$$

$$\psi_\pm(\phi) = a\exp\left[\pm i\left(\frac{2IE}{\hbar^2}\right)^{\frac{1}{2}}\phi\right]$$

Boundary condition : $\psi_\pm(\phi) = \psi_\pm(\phi + 2\pi) \Rightarrow \pm\left(\frac{2IE}{\hbar^2}\right)^{\frac{1}{2}} = m$.

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

$E_m = \dfrac{m^2\hbar^2}{2I}$, $\psi_m(\phi) = a\exp(im\phi)$ quantized.

normalization.

$$\int_0^{2\pi} a^2\, d\phi = 1. \Rightarrow a = \sqrt{\frac{1}{2\pi}}$$

$\psi_{|m|}, \psi_{-|m|}$: degenerated $\Rightarrow$ Left, Right rotation.

$$\hat{P}_\phi = -i\hbar\frac{\partial}{\partial\phi}$$

$$\hat{P}_\phi\psi_m = -i\hbar\frac{\partial\psi_m(\phi)}{\partial\phi} = \underbrace{m\hbar}_{\text{Eigen value}}\psi_m(\phi) \rightarrow \text{Eigen state of angular momentum.}$$

$$\Rightarrow [\hat{H}, \hat{P}_\phi] = 0$$

$$\psi_m^+ = \frac{1}{\sqrt{2}}(\psi_m + \psi_{-m}) = \sqrt{2}\,a\cos(m\phi)$$

$$\psi_m^- = \frac{-i}{\sqrt{2}}(\psi_m - \psi_{-m}) = \sqrt{2}\,a\sin(m\phi)$$

Separate variables,

$$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$ Plugging-in this for ☆

$$\Rightarrow \quad \frac{d^2\Phi(\phi)}{d\phi^2} = -m^2\Phi$$

$$-\sin^{-1}\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m^2}{\sin^2\theta}\Theta = \frac{2IE}{\hbar^2}\Theta$$

$$\Phi_m(\phi) = \sqrt{\frac{1}{2\pi}}\exp(im\phi) \quad (m = 0, \pm1, \pm2, \cdots)$$ See the previous page!

For the case, $m \neq \pm(2IE/\hbar^2)^{1/2}$

Replacing $\cos\theta = y$. $\Theta(\theta) \to P(y)$, $2IE/\hbar^2 = l(l+1) = \lambda$.

$$dy = -\sin\theta d\theta, \quad \frac{df}{d\theta} = \frac{df}{dy}\cdot\frac{dy}{d\theta} \Rightarrow \frac{d}{d\theta} = -\sin\theta\frac{d}{dy}.$$

$$y^2 = \cos^2\theta = 1-\sin^2\theta, \quad 1-y^2 = 1-\cos^2\theta = \sin^2\theta$$

$$\frac{d}{dy}\left[(1-y^2)\frac{dP(y)}{dy}\right] + \left(\lambda - \frac{m^2}{1-y^2}\right)P(y) = 0$$

$$\Rightarrow \quad (1-y^2)\frac{d^2P}{dy^2} - 2y\frac{dP}{dy} + \left\{\lambda - \frac{m^2}{1-y^2}\right\}P = 0.$$

(Associated Legendre derivative eq.)

$m = 0$, $P(y) = \sum_l a_l y^l$

$$(l+1)(l+2)a_{l+2}y^l - l(l-1)a_l y^l - 2la_l y^l + \lambda a_l y^l = 0.$$

$$\Rightarrow a_{l+2} = \frac{l(l+1)-\lambda}{(l+1)(l+2)}a_l$$

Solutions exist under the conditions

$$l = 0, 1, 2, \cdots, \quad |m| < l \Leftrightarrow -l < m < l$$

Order of derivative. $2l > l+m$

$$\Theta_{lm}(\theta) = \underbrace{(-1)^{\frac{m+|m|}{2}}\sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}}_{\text{Factor of angular momentum}}\ \underbrace{\frac{(1-\cos^2\theta)^{\frac{|m|}{2}}}{2^l\cdot l!}\frac{d^{l+|m|}}{d\cos^{l+|m|}\theta}(\cos^2\theta-1)^l}_{=P_l^{|m|}(\cos\theta)\ \text{Legendre polynomial}}$$

$$\int_{-1}^{1}P_l^{|m|}(\cos\theta)P_{l'}^{|m|}(\cos\theta)\,d\cos\theta = \begin{cases} 0 & (l = l') \\ \dfrac{2}{2l+1}\dfrac{(l+|m|)!}{(l-|m|)!} & (l \neq l') \end{cases}$$

- Radiative transition

E_m —— ψ_m $\quad \Psi_m = \psi_m \exp\left(-i\frac{E_m}{\hbar}t\right)$ Time-varying $\omega = \frac{E_m}{\hbar}$, $\nu = \frac{E_m}{h}$

E_n —— ψ_n $\quad \Psi_n = \psi_n \exp\left(-i\frac{E_n}{\hbar}t\right)$

$$\langle x\rangle = \int_{-\infty}^{\infty} x\,\Psi_n^*\Psi_n\,dx = \int_{-\infty}^{\infty} x\,\psi_n^*\psi_n \exp[(iE_n/\hbar)t-(iE_n/\hbar)t]\,dx$$

$$= \int_{-\infty}^{\infty} x\,\psi_n^*\psi_n\,dx$$

(Stationary state)

$\Rightarrow$ no oscillation $\Rightarrow$ no radiation

Consider an electron shift from one energy state to another

$\Psi = a\Psi_n + b\Psi_m$ The wave function of an electron that can exist in both states n and m.

$a^*a + b^*b = 1$.

When it is in the midst of the transition from m> to n>, EM waves are produced.

$$\langle x\rangle = \int_{-\infty}^{\infty} x\,(a^*\Psi_n^* + b^*\Psi_m^*)(a\Psi_n + b\Psi_m)\,dx$$

$$= a^2\int_{-\infty}^{\infty} x\,\psi_n^*\psi_n\,dx + b^*a\int_{-\infty}^{\infty} x\,\psi_m^* e^{+(iE_m/\hbar)t}\,\psi_n e^{-(iE_n/\hbar)t}\,dx$$

$$+ a^*b\int_{-\infty}^{\infty} x\,\psi_n^* e^{+(iE_n/\hbar)t}\,\psi_m e^{-(iE_m/\hbar)t}\,dx + b^2\int_{-\infty}^{\infty} x\,\psi_m^*\psi_m\,dx$$

$$\cos\left(\frac{E_m-E_n}{\hbar}\right)t\int_{-\infty}^{\infty} x\,[b^*a\,\psi_m^*\psi_n + a^*b\,\psi_n^*\psi_m]\,dx$$

$$+ i\sin\left(\frac{E_m-E_n}{\hbar}\right)t\int_{-\infty}^{\infty} x\,[b^*a\,\psi_m^*\psi_n - a^*b\,\psi_n^*\psi_m]\,dx$$

An electron undergoing a transition b/w the states n> $\leftrightarrow$ m>

$$\cos\left(\frac{E_m-E_n}{\hbar}\right)t = \cos 2\pi\left(\frac{E_m-E_n}{h}\right)t = \cos 2\pi\nu t$$

oscillates with ν.

$\Rightarrow$ dipole $\Rightarrow$ radiates

- Selection rules of electron transition in the hydrogen atom

$\int x \psi_m^* \psi_n \, dx \neq 0$ The condition necessary for an atom to radiate

$$\psi_{n,l,m} \rightarrow \psi_{n',l',m'}$$

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

$$Y_{l,m}(\theta,\phi) = c_{l,m} P_l^{|m|}(\cos\theta) e^{im\phi}$$

normalization const. Associated Legendre polynomial

Dipole moment $\mu_{n',l',m' \leftarrow n,l,m}$

$$\mu_{n'l'm' \leftarrow nlm} = \int \psi_{n'l'm'}^* \mu \psi_{nlm} \, d\tau = -e \int \psi_{n'l'm'} r \psi_{nlm} \, d\tau$$

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$
$$d\tau = r^2 dr \sin\theta \, d\theta \, d\phi$$

Transition along z

$$\mu^z = -e c_{lm}^2 \int_0^\infty R_{n'l'} R_{nl} r^3 dr \neq 0$$

$$\times \int_0^\pi P_{l'}^{|m'|} \cdot \cos\theta \cdot P_l^{|m|} \cdot \sin\theta \, d\theta \int_0^{2\pi} e^{i(m'-m)\phi} d\phi$$

$$\cos\theta P_l^{|m|}(\cos\theta) = \frac{l-|m|+1}{2l+1} P_{l+1}^{|m|}(\cos\theta) + \frac{l+|m|}{2l+1} P_{l-1}^{|m|}(\cos\theta)$$

$$\Rightarrow \frac{l-|m|+1}{2l+1} \int_0^\pi P_{l'}^{|m'|}(\cos\theta) \cdot P_{l+1}^{|m|}(\cos\theta) \cdot \sin\theta \, d\theta$$

$$+ \frac{l+|m|}{2l+1} \int_0^\pi P_{l'}^{|m'|}(\cos\theta) \cdot P_{l-1}^{|m|}(\cos\theta) \cdot \sin\theta \, d\theta$$

$z = \cos\theta$

$$= \frac{l-|m|+1}{2l+1} \int_{-1}^1 P_{l'}^{|m'|}(z) P_{l+1}^{|m|}(z) \, dz + \frac{l+|m|}{2l+1} \int_{-1}^1 P_{l'}^{|m'|}(z) \cdot P_{l-1}^{|m|}(z) \, dz \neq 0$$

$\Rightarrow$ $l' = l \pm 1$ & $|m'| = |m|$

$\int_0^{2\pi} e^{i(m'-m)\phi} d\phi \neq 0 \Rightarrow m' = m$ Only when $m' = m$.

Transitions along x, y

$$\int_0^{\pi} P_{l'}^{|m|}(\cos\theta)\cdot\sin\theta\, P_l^{|m|}(\cos\theta)\cdot\sin\theta\, d\theta$$

$$\sin\theta\, P_l^{|m|}(\cos\theta) = \frac{1}{2l+1}\left\{P_{l+1}^{|m|+1}(\cos\theta) - P_{l-1}^{|m|+1}(\cos\theta)\right\}$$

$$= \frac{1}{2l+1}\int_0^{\pi} P_{l'}^{|m'|}(\cos\theta)\left\{P_{l+1}^{|m|+1}(\cos\theta) - P_{l-1}^{|m|+1}(\cos\theta)\right\}\sin\theta\cdot d\theta$$

$$\Rightarrow \quad l' = l \pm 1 \quad \& \quad |m'| = |m| + 1$$

$\mu^{x,y}(\phi)$

$$x: \quad \int_0^{2\pi} \cos\phi\, e^{i(m'-m)\phi} d\phi = \frac{1}{2}\left(\int_0^{2\pi} e^{i(m'-m+1)\phi} d\phi + \int_0^{2\pi} e^{i(m'-m-1)\phi} d\phi\right)$$

$$y: \quad \int_0^{2\pi} \sin\phi\, e^{i(m'-m)\phi} d\phi = \frac{1}{2}\left(\int_0^{2\pi} e^{i(m'-m+1)} d\phi - \int_0^{2\pi} e^{i(m'-m-1)\phi} d\phi\right)$$

$$\Rightarrow \quad m' = m \pm 1$$

$$\Delta l = \pm 1 \quad \& \quad \Delta m = 0, \pm 1$$