Lec 20

Particle in a 1D box

→ ground state ($n=1$)

: wave function $\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$

Calculate $\langle x \rangle$, $\langle x^2 \rangle$, $\langle P \rangle$, $\langle P^2 \rangle$

$$\langle (\Delta x)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$$

$$\langle (\Delta P)^2 \rangle = \langle P^2 \rangle - \langle P \rangle^2$$

Note : $\langle A \rangle = \dfrac{\int_x \psi^*(x) \hat{A} \psi(x) \, dx}{\int_x \psi^*(x) \psi(x) \, dx}$

$$\langle x \rangle = \frac{\int_0^L \frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right) x \, dx}{\int_0^L \frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right) dx} = \frac{I_1}{I_2}$$

$$I_2 = \frac{2}{L} \cdot \frac{1}{2} \int_0^L \left[1 - \cos\frac{2\pi x}{L}\right] dx$$

$$= \frac{1}{L} \int_0^L \left(1 - \cos\frac{2\pi x}{L}\right) dx$$

$$= \frac{1}{L} \left\{ [x]_0^L - \left[\frac{\sin\frac{2\pi x}{L}}{\frac{2\pi}{L}}\right]_0^L \right\}$$

$$= \frac{1}{L} \left\{ L - \frac{L}{2\pi} \sin 2\pi \right\} = 1$$

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$$I_1 = \int_0^L \frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right) x \, dx$$

$$= \frac{2}{L}\left[\left[x \int \sin^2\left(\frac{\pi x}{L}\right) dx \right]_0^L - \int_0^L \int \sin^2\left(\frac{\pi x}{L}\right) dx \, . \, dx \right]$$

$$= \frac{2}{L}\left[\left[\frac{x}{2}\left(x - \frac{\sin \frac{2\pi x}{L}}{\frac{2\pi}{L}} \right) \right]_0^L - \int_0^L \left(\frac{x}{2} - \frac{1}{2} \frac{\sin \frac{2\pi x}{L}}{\frac{2\pi}{L}} \right) dx \right]$$

$$= \frac{2}{L}\left[\frac{L}{2}\left(L - 0 \right) - \left[\frac{x^2}{4} + \frac{1}{2} \frac{\cos \frac{2\pi x}{L}}{\left(\frac{2\pi}{L}\right)^2} \right]_0^L \right]$$

$$= \frac{2}{L}\left[\frac{L^2}{2} - \frac{L^2}{4} - \cancel{\frac{1}{2} \cdot \frac{L^2}{4\pi^2}} + \cancel{\frac{1}{2} \frac{L^2}{4\pi^2}} \right]$$

$$= \frac{2}{L} \times \frac{L^2}{4} = \frac{L}{2}$$

$$\langle x^2 \rangle = \int_0^L x^2 \sin^2\left(\frac{\pi x}{L}\right) dx = \frac{L^2}{6}\left(2 - \frac{3}{\pi^2} \right)$$

$$\langle P \rangle = \int_0^L \psi^*(x) \left(-i h \frac{\partial}{\partial x} \psi(x) \right)$$

$$\frac{2}{L} \int_0^L \left(\frac{\pi x}{L}\right) \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right) . \frac{\pi}{L} \, dx$$

$$-ih \frac{2}{L} . \frac{\pi}{L} \int_0^L \cos\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) dx$$

$$\frac{-ih\pi}{L^2} \int_0^L \sin\left(\frac{2\pi x}{L}\right) dx = -\frac{i\pi h}{L^2} \left[\frac{\cos \frac{2\pi x}{L}}{\frac{2\pi}{L}} \right]_0^L$$

$$= -\frac{i\pi h}{L^2} \left[\frac{1}{\frac{2\pi}{L}} - \frac{1}{\frac{2\pi}{L}} \right] = 0.$$

$$\langle P^2 \rangle = \frac{h^2}{4L^2}$$

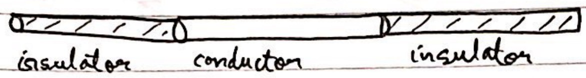
$$\Delta x \equiv \text{Uncertainty in } x$$

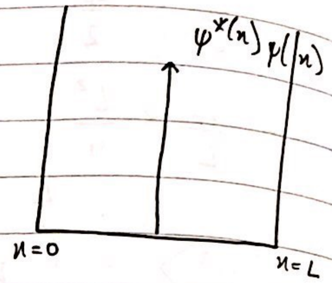
$$= \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

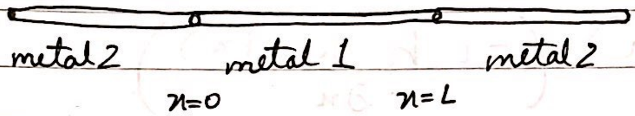
$$\Delta p \equiv \text{Uncertainty in } p$$

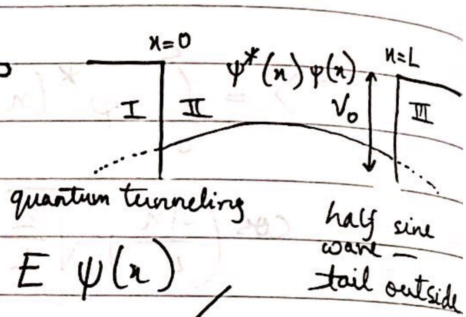
$$= \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$

$$\Delta x \cdot \Delta p \geq \hbar/2 \text{ — Uncertainty Principle.}$$









$$E < V_0, \quad \hat{H}\psi(x) = E\,\psi(x)$$

$$E > V_0.$$

scanning tunneling microscopy (STM)

10^{-6} m $\rightsquigarrow$ 10^{-9} m

Region I : $U(x) = 0$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_I(x) = E\,\psi(x)$$

$$\Rightarrow \psi_I(x) = C_1 e^{k_1 x} \qquad k_1 = \sqrt{\frac{2m|E|}{\hbar^2}}$$

$$\psi_{III}(x) = C_3 e^{-k_1 x}$$

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Page

Boundary Conditions

$$\psi_I (x = -a) = \psi_2 (x = -a)$$

[ψ should be single valued]

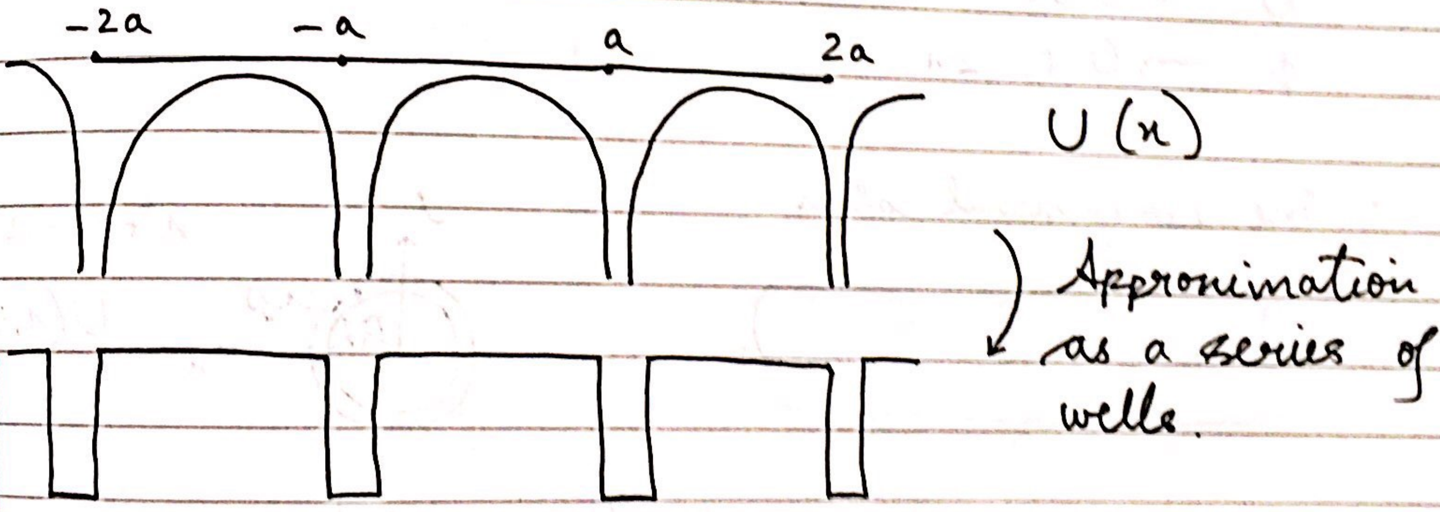
$$\frac{d}{dx}\psi_I (x = -a) = \frac{d}{dx}\psi_{II}(x = -a)$$

[ψ should be continuously differentiable]

Similarly :

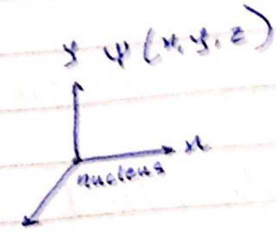
$$\psi_{II}(x = a) = \psi_{III}(x = a)$$

$$\frac{d}{dx}\psi_{II}(x = a) = \frac{d}{dx}\psi_{II}(x = a)$$



Lec 21

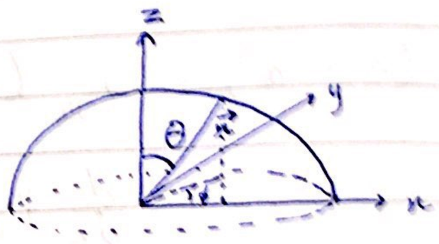
Atoms



$\psi^*(x,y,z)\,\psi(x,y,z)$: Probability density of finding electron at (x,y,z)

Potential energy $U(x,y,z) \neq 0$.
:- electron-nucleus interaction is not zero.

$\psi(x,y,z) \rightsquigarrow \psi(r,\theta,\phi)$

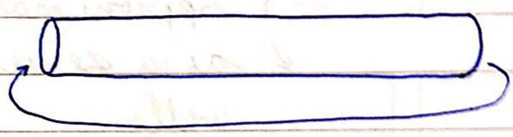


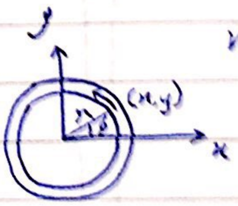
$r \to 0$ to ∞

$\theta \to 0$ to π

$\phi \to 0$ to 2π

- One-Dimensional atom





$x^2 + y^2 = r^2$

$U(x,y) = 0$

Schrodinger Equation : $-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right]\psi(x,y) = E\,\psi(x$

Cartesian to Polar : $x = r\cos\phi$, $y = r\sin\phi$

r is a constant

$\phi \in [0, 2\pi)$

$$\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right] = \left[\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right.$$

To Derive:

$$\frac{\partial f(x,y)}{\partial r} = \frac{\partial f}{\partial x} \cdot \frac{\partial x}{\partial r} + \frac{\partial f}{\partial y} \cdot \frac{\partial y}{\partial r}$$

- for this problem: r is fixed.

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{r^2} \cdot \frac{\partial^2}{\partial \phi^2}$$

Schrodinger equation in polar coordinates:

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \psi(r,\phi) = E \cdot \psi(r,\phi)$$

$$|||$$

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \Phi(\phi) = E\,\Phi(\phi)$$

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

$I = mr^2 \Rightarrow$ Moment of Inertia

$$\therefore -\frac{\hbar^2}{2I} \cdot \frac{\partial^2}{\partial \phi^2} \Phi(\phi) = E\,\Phi(\phi)$$

$$\frac{\partial^2}{\partial \phi^2} \Phi(\psi) = -\frac{2IE}{\hbar^2} \Phi(\phi)$$

$\rightarrow$ general solution $\Phi(\phi) = Ae^{im_l \phi}$

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

$$Ae^{im_l(\phi + 2\pi)} = Ae^{im_l \phi}$$

$$e^{im_l 2\pi} = 1 \; ; \; m_l = 0, \pm 1, \pm 2, \pm 3, \ldots$$

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Substitute : $\Phi(\phi) = Ae^{im_l \phi}$ in the Schrodinger equation & determine E.

$$\Rightarrow E_{m_l} = \frac{m_l \hbar^2}{2I} \qquad m_l = 0, \pm 1, \pm 2, \ldots$$

$m_l = \pm 2$ 2nd excited

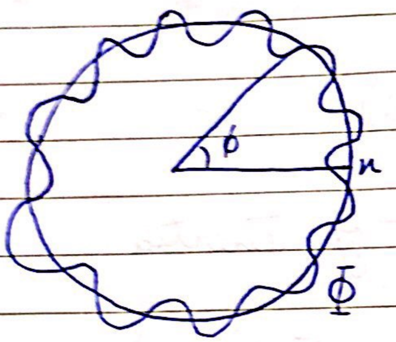
$m_l = \pm 1$ 1st excited

$E_{m_l} = 0$ $m_l = 0$ ground

find A : normalize $\Phi(\phi) = Ae^{im_l \phi}$

$$\int_0^{2\pi} \Phi^*(x)\, \Phi(x)\, dx = 1 \longrightarrow A = \frac{1}{\sqrt{2\pi}}$$

$$\therefore \Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l \phi} \; ; \; m_l = 0, \pm 1, \pm 2, \ldots$$



- Angular Momentum.

$$\vec{L} = \vec{r} \times \vec{P}$$

$$\hat{i} L_x + \hat{j} L_y + \hat{k} L_z = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ P_x & P_y & P_z \end{vmatrix}$$

$$L_z = x P_y - y P_x , \quad \hat{L}_z = \hat{x}\left(-i\hbar \frac{\partial}{\partial y}\right) - \hat{y}\left(-i\hbar \frac{\partial}{\partial x}\right)$$

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

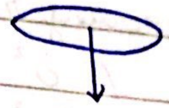
$\hat{L}_z \, \Phi(\phi) = m_l \hbar \, \Phi(\phi)$

Angular Momentum $= m_l \hbar$

↳ quantised

$m_l = 0, \pm 1, \pm 2, \ldots$

$m_l > 0$



$m_l < 0.$

· Particle on a sphere

Angular Momentum quantum number

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

$m_l = 0, \pm 1, \ldots, \pm l, \ldots$

$r \to$ fixed

$\theta \to 0$ to π

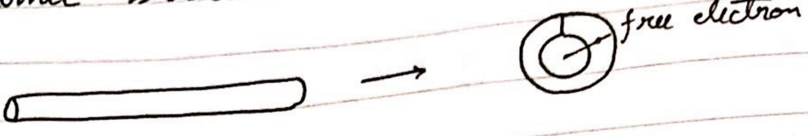
$\phi \to 0$ to 2π

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\psi(x,y,z)$$

$$= E\psi(x,y,z)$$

Lec 22 Atomic Structure / Spectra.

Recap:



1) Polar : $(x, y) \rightarrow (r, \phi)$

2) $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \rightarrow \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$

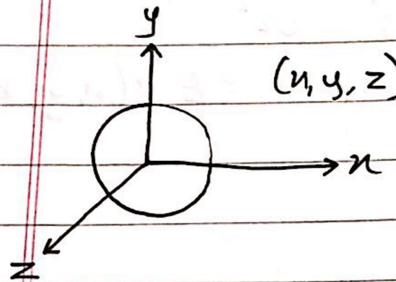
3) → Schrodinger equation in polar coordinates :

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)\Phi(\phi) = E\,\Phi(\phi)$$

4) Apply the boundary condition : $\Phi(\phi + 2\pi) = \Phi(\phi)$

$\Rightarrow \Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$, m being the magnetic quantum number.

- Particle on a sphere of radius r.



$(x, y, z) \rightsquigarrow (r, \theta, \phi)$

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

Step 1 : express : $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

in terms of r, θ, ϕ.

Step 2 : rewrite the schrodinger equation in terms of r, θ, ϕ.

$$\nabla^2 = \cancel{\frac{\partial^2}{\partial r^2}} + \frac{2}{r}\cancel{\frac{\partial}{\partial r}} + \frac{1}{r^2}\Lambda^2$$

$$\Lambda^2 \equiv \frac{1}{\sin^2\theta}\frac{\partial}{\partial \phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right)$$

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Schrodinger equation

$$\Lambda^2 \psi(r, \theta, \phi) = -\left(\frac{2IE}{\hbar^2}\right) \psi(r, \theta, \phi)$$

$I = mr^2$

Solution : Spherical harmonics $Y_{lm}(\theta, \phi)$
↳ 2 quantum numbers : l, m

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}} \cdot P_{lm}(\cos\theta)\, e^{im\phi}$$

$$\psi(r, \theta, \phi) = Y_{lm}(\theta, \phi)$$

- here $P_{lm}(\cos\theta)$ is called the associated Legendre Polynomial

$m \rightarrow$ magnetic quantum number $[0, \pm 1, \pm 2, \ldots]$

$l \rightarrow$ angular momentum quantum number $[0, 1, 2, \ldots]$

• Spherical Harmonics

l	m	$Y_{lm}(\theta, \phi)$
0	0	$1/2 \sqrt{\pi}$
1	0	$1/2 \sqrt{3\pi} \cos\theta$
1	± 1	$\mp \sqrt{\frac{3}{2\pi}} \sin\theta\, e^{\pm i\phi}$

$l = 0 \rightarrow$ s orbitals [spherical]

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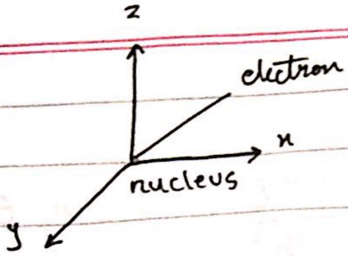
r, θ, ϕ vary

H - atom



$$U(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ [Derive]

$$\left.\begin{aligned}\rightarrow\ & -\frac{\hbar^2}{2m}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right)\psi(r,\theta,\phi) \\ \# \ & -\frac{\hbar^2}{2m}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\end{aligned}\right\} \text{Kinetic energy}$$

$$\left.-\frac{e^2}{4\pi\varepsilon_0 r}\right\} \text{Potential energy}$$

- Method of Separation of variables:

$$\psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{radial}}.\underbrace{Y(\theta,\phi)}_{\text{angular}}$$

$$\Rightarrow -\frac{\hbar^2}{2m}Y(\theta,\phi)\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}R(r)\right)\right)$$

radial + angular = 0.

↳ using the particle on a sphere model.

$Y_{lm}(\theta,\phi)$: solution to angular part

$R_{nl}(r)$:

3 quantum numbers : $n = 1, 2, 3, \ldots$

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

$m = 0, \pm 1, \pm 2, \ldots, \pm l.$

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Page

$$\psi_{nlm} = R_{nl}(r)\, Y_{lm}(\theta, \phi)$$

- Principal Quantum Number

n	l	m	ψ
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\sigma}$

1s orbital

$$\sigma = \frac{r}{a_0}, \quad a_0 = \text{Bohr Radius.}$$

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