Operators

Note Title 03-10-2009

Recap:

$$V = \begin{cases} 0 & 0 \le x \le a(L) \\ \infty & \text{otherwise} \end{cases}$$

T I S E

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi}$$

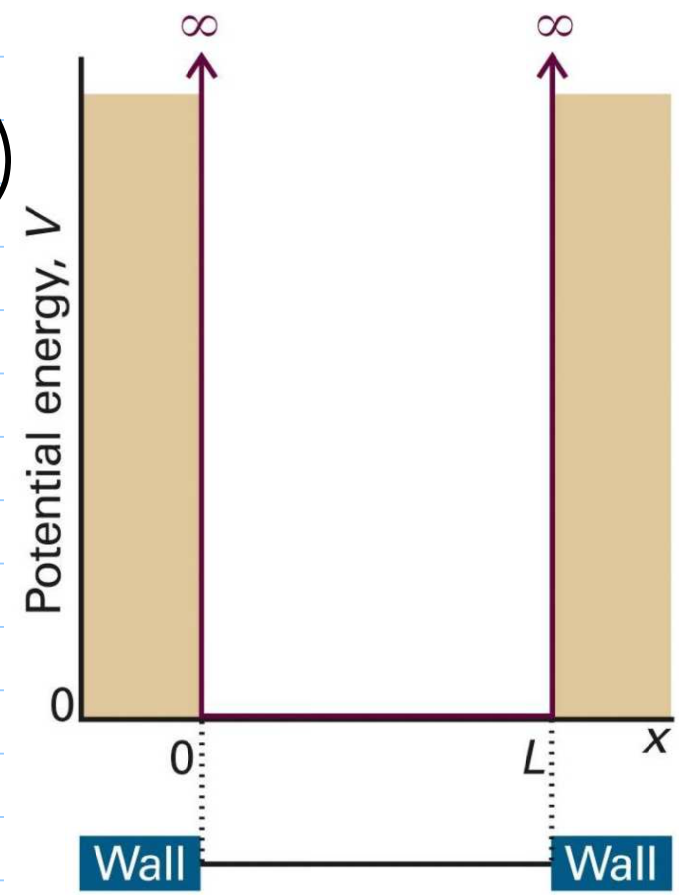

Figure 9-1
Atkins Physical Chemistry, Eighth Edition

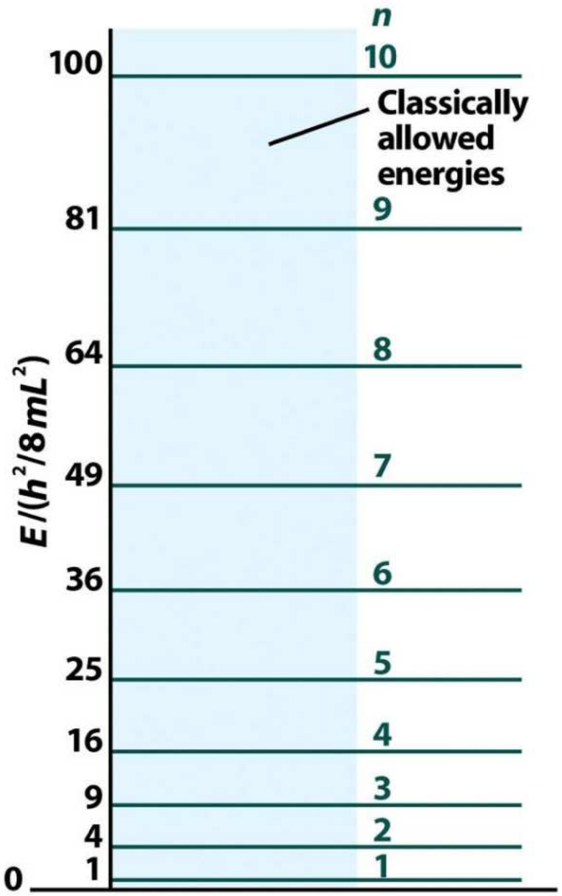

Figure 9-2
Atkins Physical Chemistry, Eighth Edition

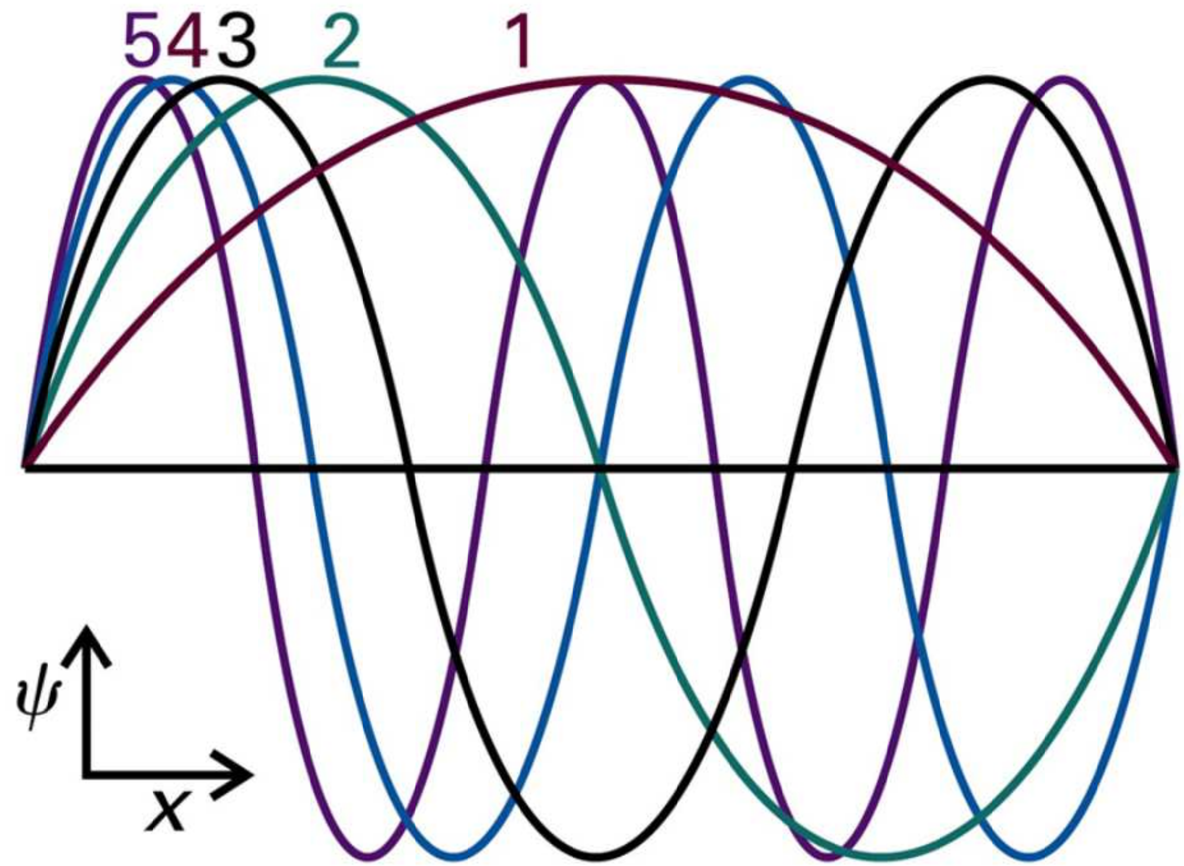

Figure 9-3
Atkins Physical Chemistry, Eighth Edition

Test yourself

For a particle in a 1D box, in which of the following states is the probability of finding the particle in the center the smallest

$\boxed{\text{(a) } n \neq 0}$ (b) n=1 (c) n=2 (d) n=3 $|\psi|^2$ $x = a/2$

For a particle in a 1D box, in which of the states
(a) n=0 (b) n=1 (c) n=2 (d) n=3
is there the greatest probability for finding the particle 1/4 of the way from either end?

ψ_i's form an "orthonormal" set

$$\underbrace{\int \psi_1^* \psi_3 \, d\tau = 0}_{\text{Scalar product}}$$

$\Rightarrow \psi_1$ & ψ_3 are $\boxed{\text{Orthogonal}}$

$\parallel^r$ $\hat{i} \cdot \hat{j} = 0 \,\|$

Gen:

$$\int \psi_i^* \psi_j \, d\tau = 0$$

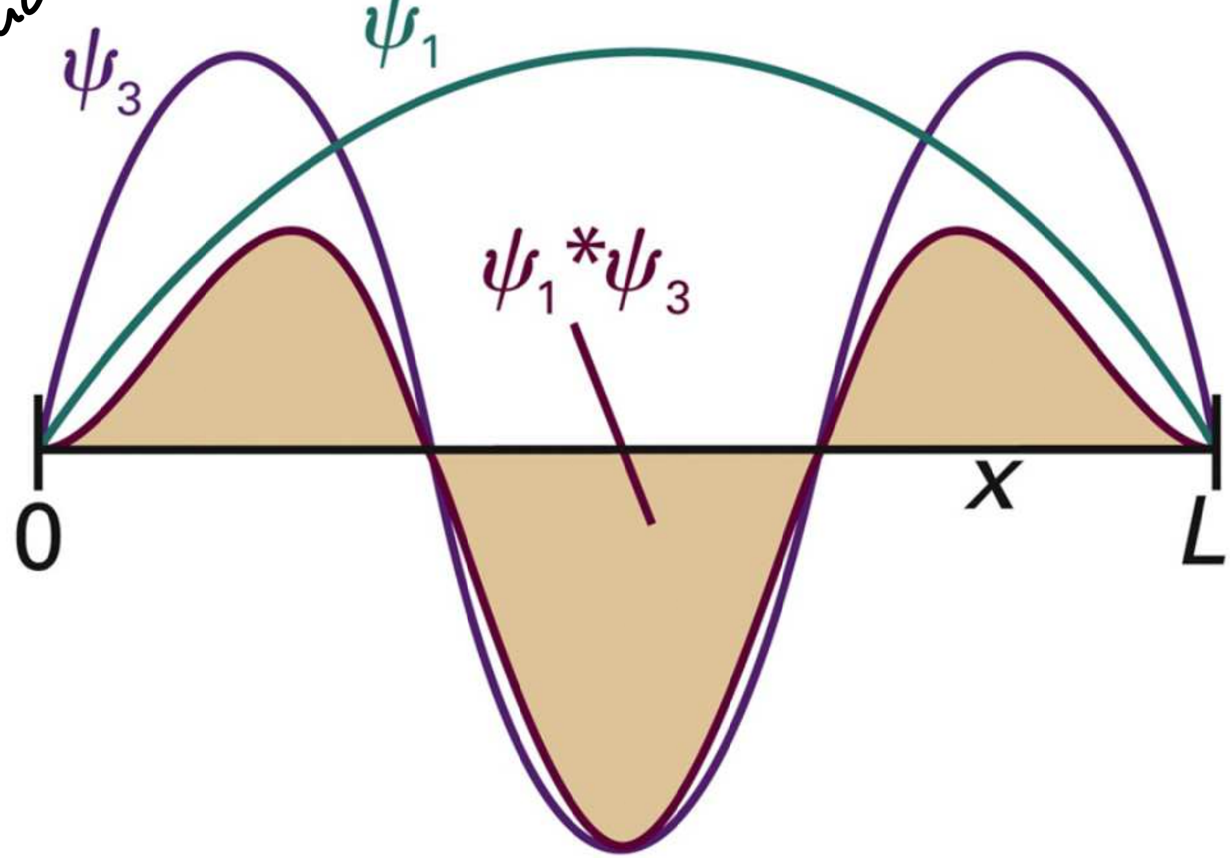

Figure 9-5
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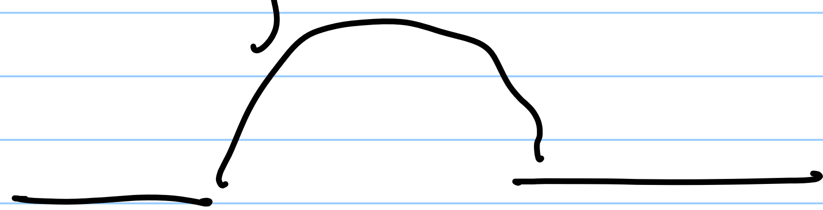
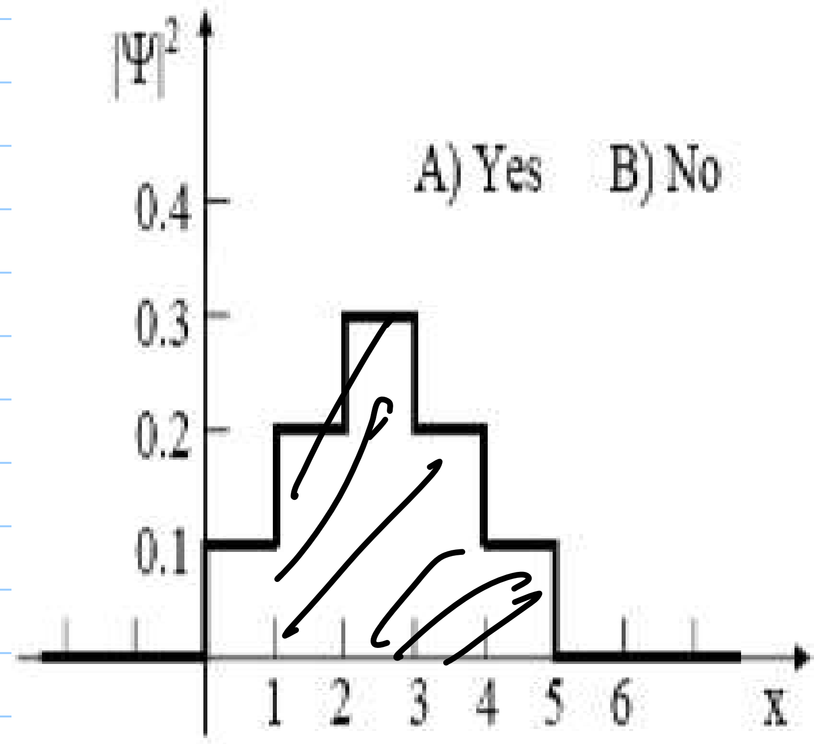
Test yourself

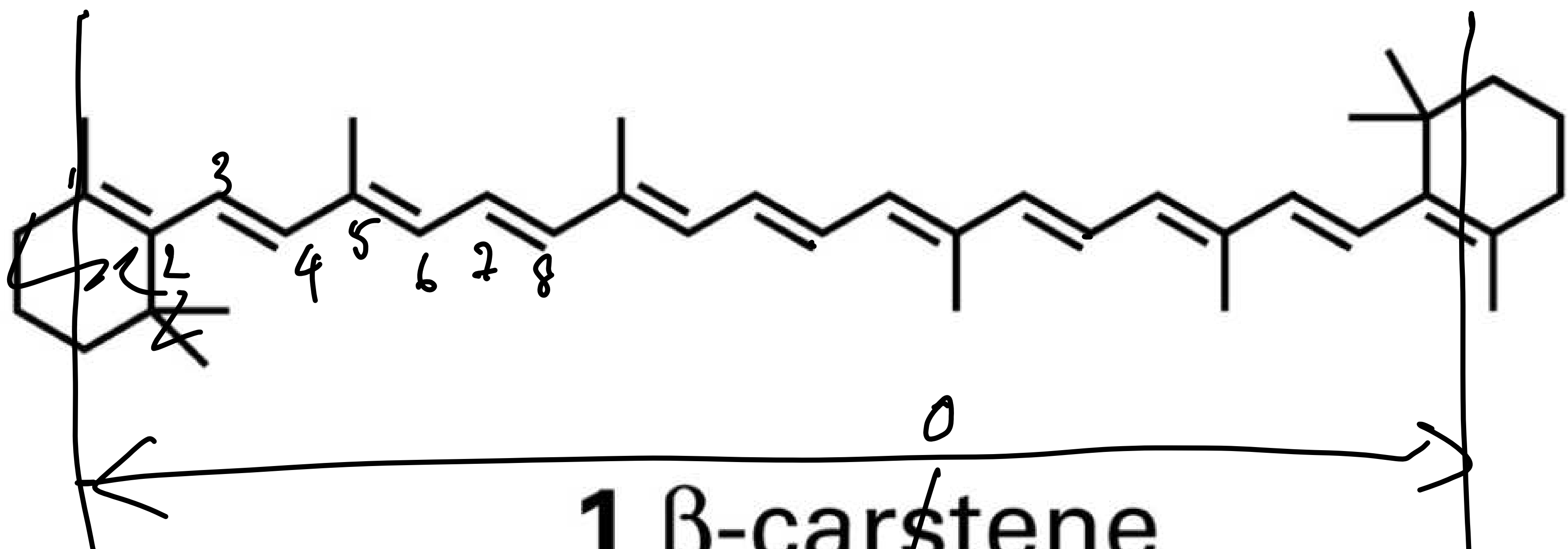
Is the wavefunction given alongside normalized?
Note that this is a plot of $|\psi|2$ vs. x.

$\int |\psi|^2 dx$





Carrots $11\, r_{C-C}$ & $11\, r_{C=C}$



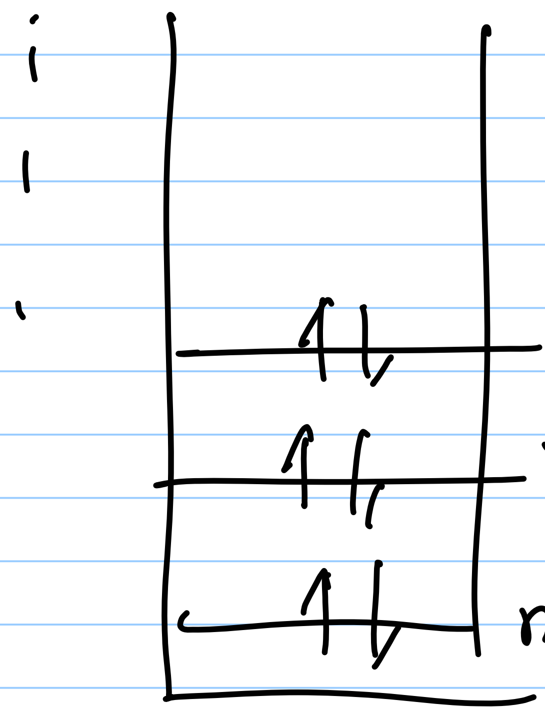
1 β-carotene

Marginal 9-1
Atkins Physical Chemistry, Eighth Edition

22 $\pi\, e^-$

$$E_n = \frac{n^2 h^2}{8ma^2}$$

$a = 11 r_{c-c} + 12 r_{c=c}$



$n = 3$

$n = 2$

$n = 1$

$22e^-$

$n = 11$

$n=11 \longrightarrow n = 12$

$\Delta E =$ 400 - 700nm

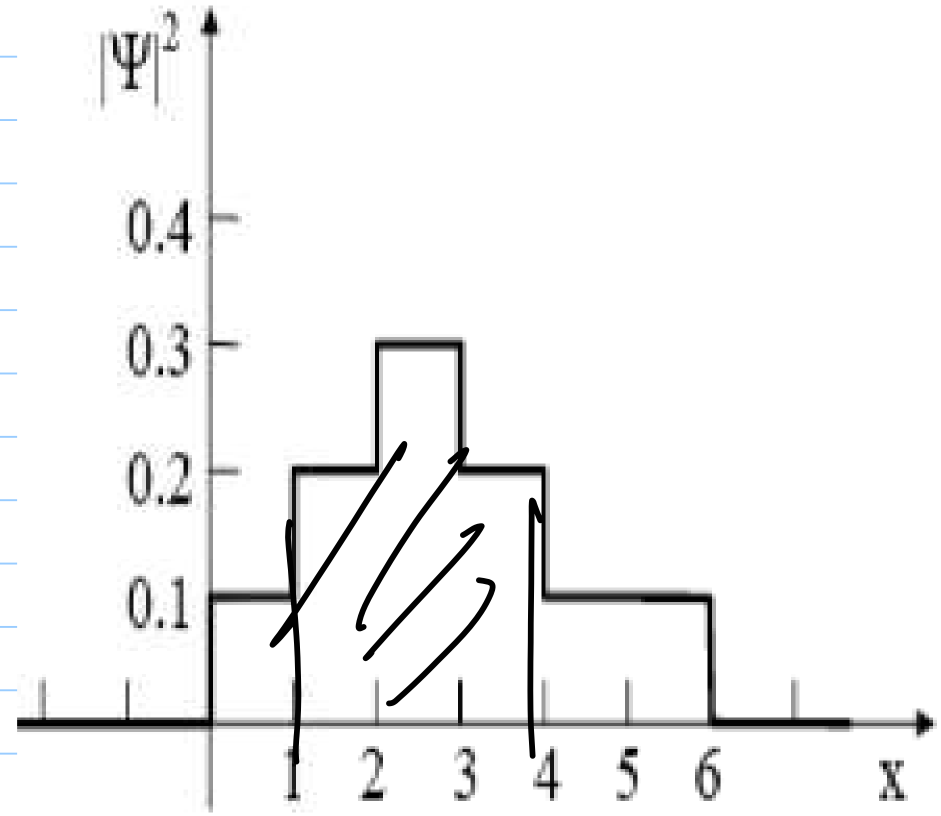
$\downarrow$

nm

Test yourself

The probability density for a normalized wavefunction is plotted below. What is the probability that a position measurement will result in a measured value between 2 and 5?

(a) 2/3 (b) 0.3 (c) 0.4 (d) 0.5 (e) 0.6



What is the average position?

$$\langle x \rangle = \int x \, |\Psi|^2 \, dx$$

$$= \int \Psi^* \, x \, \Psi \, dx$$

$$\sum$$

$$\lambda = \frac{h}{p}$$

Time independent SE

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + V\psi = E\psi$$

$$\boxed{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx} + V\right)}\psi = E\psi$$

$$\boxed{\underbrace{\hat{O}_p}_{\text{Operator}} \Psi = E \Psi}$$

$$2 \quad f(x)$$

$$\hat{O}_p \Psi = \Psi'$$

$$\hat{x}$$

$$\underbrace{x}_{\text{Multiplicative operator}} \underbrace{(x^3 - 4x^2)}_{\Psi} = x^4 - 4x^3$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$ — Kinetic energy

$$\hat{O}_p \psi = \psi' \quad \text{constant } \psi$$

$$\hat{O}_p \psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left(x^3 - 4x^2\right) = g(x)$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} A \sin\left(\frac{n\pi x}{a}\right) = \text{constant}}$$

Classical observables (position, momentum, kinetic energy, ang momentum) ...

are represented in QM by $\boxed{\text{linear, Hermitian}}$ operators

Position $\hat{x} \to x \times$

Kinetic energy $\hat{T} \to -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

Momentum

$\hat{x} \qquad \hat{y} \qquad \hat{z}$

x- Momentum $\quad -i\hbar \dfrac{\partial}{\partial x}$

y- momentum $\quad -i\hbar \dfrac{\partial}{\partial y}$

$$\hat{\vec{p}} = -i\hbar \vec{\nabla}.$$

$$\hat{T} = \frac{\hat{\vec{p}} \cdot \hat{\vec{p}}}{2} = -\frac{\hbar^2}{2m} \nabla^2$$

$V(x) = \frac{1}{2} k x^2$

$\hat{V} = \frac{1}{2} k x_x^2$

$$\vec{\hat{L}}$$

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

$$\vec{\hat{L}} = \begin{vmatrix} i & j & k \\ x & y & z \\ -i\hbar\frac{\partial}{\partial x} & -i\hbar\frac{\partial}{\partial y} & -i\hbar\frac{\partial}{\partial z} \end{vmatrix}$$

$$\boxed{x\frac{\partial}{\partial x}\psi \neq \frac{\partial}{\partial x}x\psi}$$

Linear

Superposition

$$\hat{O}_p (c_1 \psi_1 + c_2 \psi_2) = c\, \hat{O}_p \psi_1 + c_2 \hat{O}_p \psi_2$$

$$\frac{d}{dx}\left(c f(x) + d\, g(x)\right) = c \frac{d}{dx} f(x) + d \frac{d}{dx} g(x)$$

$$= c\, \hat{O}_p f + d\, O_p g$$

$$(c_1 \psi_1 + c_2 \psi_2)^2$$

$$\sqrt{(c_1 \psi_1 + c_2 \psi_2)}$$

Hermitian

$$\langle T \rangle = \int \psi^* \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \psi \, dx$$

$d\tau$

$$= \int \psi^* \hat{T} \psi \, dx$$

"Real"

$$\boxed{\int \psi^* \hat{T} \psi \, d\tau = \int (\hat{T} \psi)^* \psi \, d\tau}$$

$k =$

$$\psi = Ae^{ikx} \qquad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$$

$$\left(\int \psi^* \hat{O}_p \psi \, d\tau\right) = \left(\int \psi^* \hat{O}_p \psi \, d\tau\right)^*$$

$$= \int (\hat{O}_p \psi)^* \psi \, d\tau$$

$\hat{O}_p$ is Hermitian

$$-i\hbar \frac{\partial}{\partial x} \left(\cancel{-i\hbar \frac{\partial}{\partial x}}\right) A e^{ikx} = \overset{\times i}{-i}\hbar k$$

$$= \hbar k$$

Postulate 2:

Linear, Hermitian Operator for every classical observable

Postulate 1:

$\psi(x, t) \rightarrow$ wave function

$|\psi|^2$

Postulate 3 :

Measurement

Eigenvalues of the operator

$$\langle O_p \rangle = \frac{\int \psi^* \hat{O_p} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

$$\hat{O}_p \psi = \psi'$$

Eigenvalue equation $\boxed{\hat{O}_p \psi = \text{constant } \psi}$

ψ is an eigenfunction of $\hat{O}_p$

& constant is its eigenvalue

$$\left(\underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{\hat{T} = E} A \sin\frac{\pi x}{a}\right) = \frac{h^2}{8ma^2} A \sin\left(\frac{\pi x}{a}\right)$$

eigenfunctia

Eigenvalue

$$-i\hbar\frac{\partial}{\partial x}\,\underbrace{Ae^{ikx}} = \hbar k\, A e^{ikx}$$

eigenvalue

$$\frac{h^2}{8ma^2} \qquad \frac{4h^2}{8ma^2} \qquad \frac{9h^2}{8ma^2} \quad \ldots$$

$$\uparrow \qquad \uparrow \qquad \uparrow$$

$$\cancel{\frac{5.5\,h^2}{8ma^2}}$$

$e^{\frac{i\pi x}{a}} + e^{-\frac{i\pi x}{a}}$

$-i\hbar \frac{\partial}{\partial x} \sin\left(\frac{\pi x}{a}\right) = -i\hbar \frac{\pi}{a} \cos\left(\frac{\pi x}{a}\right)$

A

$-\hbar k \qquad \hbar k$

$\langle p_x \rangle = \int A \sin\left(\frac{\pi x}{a}\right) - i\hbar \frac{\partial}{\partial x} A \sin\left(\frac{\pi x}{a}\right) dx$

$= 0$

System

$$\psi = \sqrt{\frac{2}{a}}\left(\frac{1}{\sqrt{3}}\sin\left(\frac{\pi x}{a}\right) + \frac{1}{\sqrt{3}}\sin\left(\frac{2\pi x}{a}\right) + \frac{1}{\sqrt{3}}\sin\left(\frac{3\pi x}{a}\right)\right)$$

$$\hat{T}$$

$$\frac{1}{3}\left\{\frac{h^2}{8ma^2}\right\} \quad \frac{1}{3}\left\{\frac{4h^2}{8ma^2}\right\} \quad \frac{9h^2}{8ma^2}$$

$$\langle T\rangle = \frac{1}{3}\left\{\frac{h^2}{8ma^2} + \dots\right\}$$

Postulate 4:

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = \Big(\underbrace{-\frac{\hbar^2}{2m}\nabla^2 + V}\Big)\Psi}$$

$\Psi(x,t)$

Hamiltonian $\leftarrow \hat{\mathcal{H}} = \underline{\hat{T} + \hat{V}}$

$\hat{\mathcal{H}} \to$ Operator for total energy

Recap

1) $\Psi \rightarrow$ Probability

2) Operators $\rightarrow$ Linear Hermitic

3) Measurement $\rightarrow$ Expectation value

4) Schrödinger equation

↳ TDSE

Harmonic Oscillator