

* The Superposition Principle

(A) Time-dependent. $\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$ (Linear PDE)

~~_____~~. If $\Psi_1(t)$ and $\Psi_2(t)$ are solutions of the TDSE, then so is

any combination $A\Psi_1(t) + B\Psi_2(t)$
[if $\hat{H}\Psi_1 = i\hbar \frac{\partial \Psi_1}{\partial t}$ & $\hat{H}\Psi_2 = i\hbar \frac{\partial \Psi_2}{\partial t}$ then $\hat{H}(A\Psi_1 + B\Psi_2) = i\hbar \frac{\partial (A\Psi_1 + B\Psi_2)}{\partial t}$]

Ex! The harmonic oscillator, time-indep. solutions:
 $\phi_0(x) = e^{-x^2/2a^2}$, $\phi_1(x) = e^{-x^2/2a^2} x$
[$E_0 = \frac{1}{2}\hbar\omega$] [$E_1 = \frac{3}{2}\hbar\omega$] ...

This means, solutions of the Time-dependent SE are $\phi_0(x) e^{-iE_0 t/\hbar}$, $\phi_1(x) e^{-iE_1 t/\hbar}$

Thus, any combination
 $A\phi_0(x) e^{-iE_0 t/\hbar} + B\phi_1(x) e^{-iE_1 t/\hbar}$
 $= A\phi_0(x) e^{-i\frac{\omega}{2}t} + B\phi_1(x) e^{-i\frac{3\omega}{2}t}$

is a solution of the TDSE.

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(B) Time-independent $\hat{H}\Psi = E\Psi$

[Reminder: solutions are stationary states; if ϕ_0 is a solution, then $\phi_0 e^{-iEt/\hbar}$ is a solⁿ of the TDSE $\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$]

If Ψ_1 and Ψ_2 are solutions corresponding to the SAME E , then $A\Psi_1 + B\Psi_2$ is also solution.

$$\hat{H}\Psi_1 = E\Psi_1, \hat{H}\Psi_2 = E\Psi_2 \Rightarrow \hat{H}(A\Psi_1 + B\Psi_2) = E(A\Psi_1 + B\Psi_2)$$

~~Ex!~~ $\hat{H} = i\hbar \frac{\partial^2 \Psi}{\partial x^2}$ (single pole in 1D region)

$\sin kx, \cos kx$ are solutions, with $E = \frac{\hbar^2 k^2}{2m}$

$\Rightarrow A \sin kx + B \cos kx$ is also solution.

BUT $\sin k_1 x, \cos k_2 x$ are solutions, but

$A \sin k_1 x + B \cos k_2 x$ is not a solution

if $k_1 \neq k_2$!

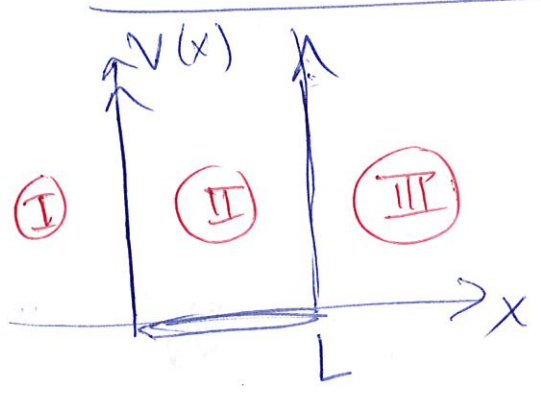
$$\hat{H}\Psi_1 = \frac{\hbar^2 k_1^2}{2m} \Psi_1, \hat{H}\Psi_2 = \frac{\hbar^2 k_2^2}{2m} \Psi_2$$

SKIP

$$\Rightarrow \hat{H}(A\psi_1 + B\psi_2) = \frac{\hbar^2}{2m} (k_1^2 A\psi_1 + k_2^2 B\psi_2) \neq E (A\psi_1 + B\psi_2)$$

⇒ Superposition not a solution if corresponding to different energies.

* PARTICLE in 1D BOX (infinite SQUARE WELL)

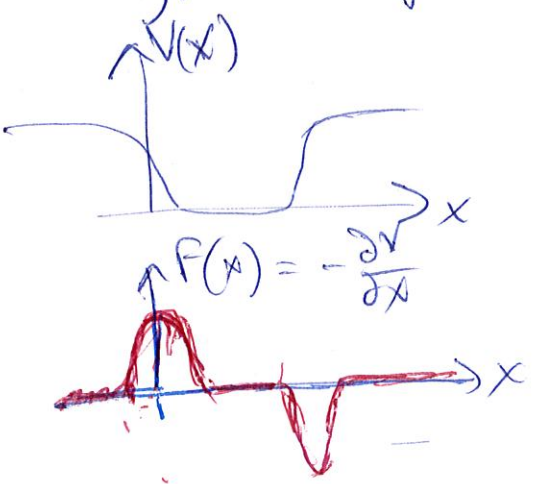


$$V(x) = \begin{cases} \infty & x \leq 0 & \text{Region I} \\ 0 & x \in (0, L) & \text{Region II} \\ \infty & x \geq L & \text{Region III} \end{cases}$$

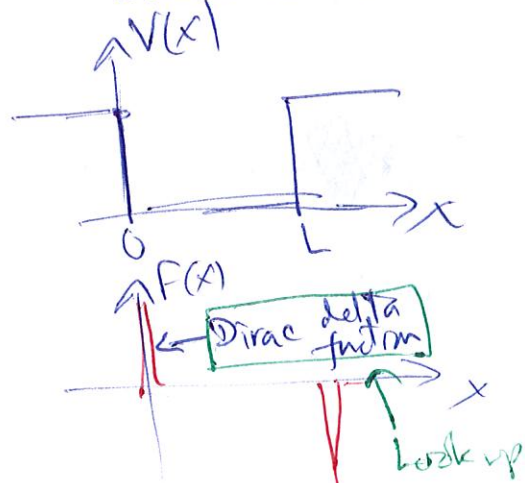
i.e., particle sharply confined to region II.

Motivation: where does this come from?

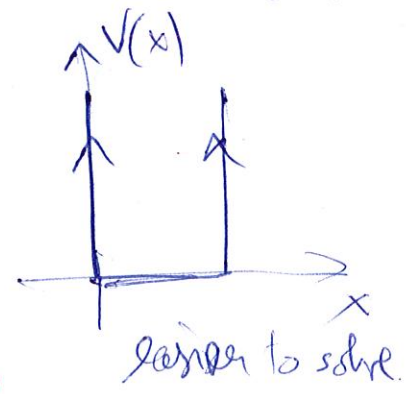
Typical "confinement":



Idealization!



Further idealization!



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Looking for stationary states $\Psi_n(x)$ of energy E_n !

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi_n(x)}{dx^2} + V(x) \Psi_n(x) = E_n \Psi_n(x)$$

[Time-evolving states, solutions of TDSE? Too difficult]

In regions I and III, if $\Psi_n(x)$ is nonzero, then

finite + ∞ , finite = finite \Rightarrow inconsistent

$\Rightarrow \Psi_n(x) = 0$ for $x \leq 0$ & $x \geq L$ (outside box)

Inside, $\Psi_n(x)$ satisfies

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi_n}{dx^2} = E_n \Psi_n(x) \Rightarrow \frac{d^2 \Psi_n}{dx^2} + \left(\frac{2mE_n}{\hbar^2} \right) \Psi_n = 0$$

Let's rename $k_n = \frac{2mE_n}{\hbar^2}$: $\Psi_n''(x) + k_n^2 \Psi_n = 0$

Familiar: like classical eq. for simple harmonic

motion: $\frac{d^2 z}{dt^2} + \omega^2 z = 0$, follows from $m \frac{d^2 z}{dt^2} = F = -m\omega^2 z$

except: t, ω replaced by x, k_n

Classical H.O. has solutions $z = A \sin \omega t + B \cos \omega t$

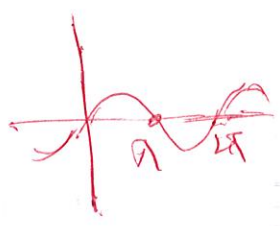
We thus have solutions for particle in box

$$\Psi_n(x) = A \sin(k_n x) + B \cos(k_n x)$$

If box were infinite, any solution would've been allowed. But for finite box we have BOUNDARY CONDITIONS:

$$\Psi_n(0) = 0, \quad \Psi_n(L) = 0$$

$$\Rightarrow B = 0 \quad \text{and} \quad \sin(k_n L) = 0$$



Allowed values of k_n :

$$k_n L = 0, \pi, 2\pi, \dots \Rightarrow k_n = 0, \frac{\pi}{L}, \frac{2\pi}{L}, \dots$$

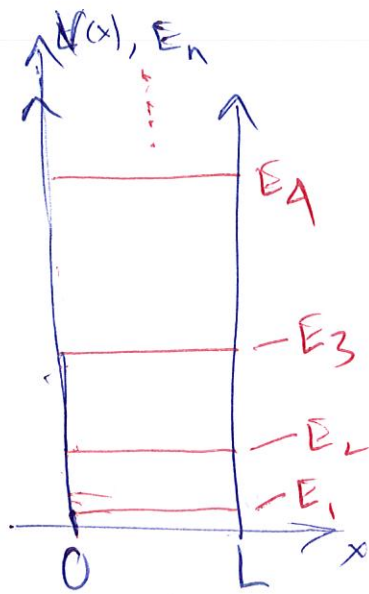
~~...~~ $k_n = 0$ corresponds to $\Psi_n = 0$ everywhere \rightarrow not meaningful.

Allowed values of $E_n = \frac{\hbar^2 k_n^2}{2m}$

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2} \quad n = 1, 2, 3, \dots$$

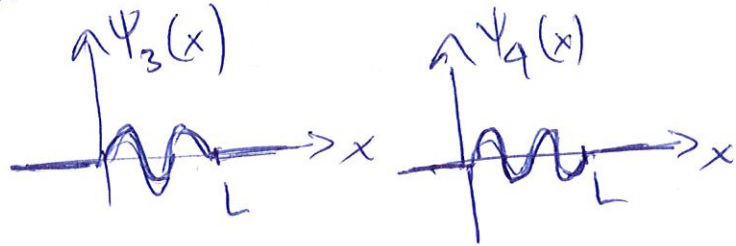
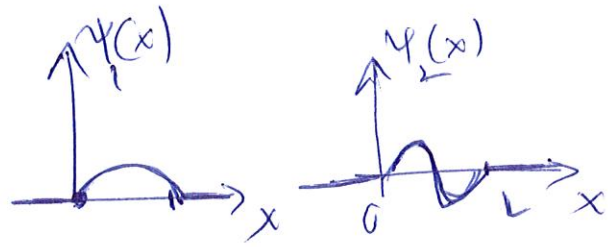
Corresponding eigenfunctions: $\Psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right)$

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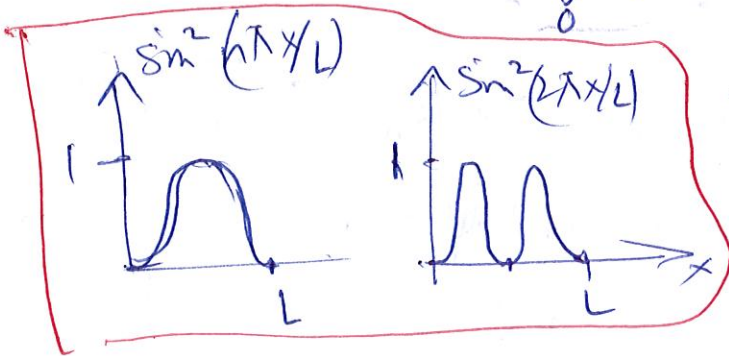
Corresponding w.f.'s

$$E_n \propto n^2$$



More and more nodes in higher-energy wavefunctions.

Normalization: $\int_0^L |\psi_n(x)|^2 dx = |A|^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$



$$= |A|^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = |A|^2 \cdot L/2 \quad (\text{indep. of } n)$$

$$\Rightarrow A = \sqrt{\frac{2}{L}} \quad (\text{can choose to be real/positive})$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\sqrt{\frac{2mE_n}{\hbar^2}} x\right) = \sqrt{\frac{2}{L}} \sin(k_n x)$$

$$E_n = \frac{\hbar^2 k_n^2}{2m}$$

↑
arbitrary sign/phase

Time-dependent SE solutions: $\psi_n(x,t) = \sqrt{\frac{2}{L}} \sin(k_n x) e^{-iEt/\hbar}$

Lowest-energy state is called GROUND STATE

G.S. energy = $\frac{\hbar^2 \pi^2}{2mL^2}$ G.S. wavefunction $\Psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$

* Why is g.s. energy not zero?

Because of uncertainty principle.

Position uncertainty $\sim L$

\Rightarrow Momentum uncertainty $\sim \frac{\hbar}{L}$

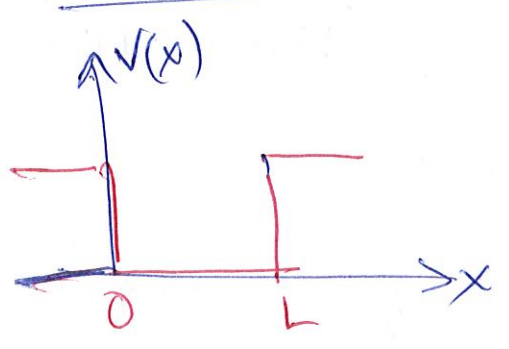
(\sim means up to a dimensionless factor)

Thus energy (classically $E = \frac{p^2}{2m}$) is expected

to be not smaller than $\sim \frac{(\hbar/L)^2}{2m} \sim \frac{\hbar^2}{mL^2}$

\rightarrow NORMALIZATION (next page)

* Finite SQUARE WELL



$$V(x) = \begin{cases} V_0 & \text{if } x \leq 0 \text{ Region I} \\ 0 & \text{if } x \in (0, L) \text{ Reg. II} \\ V_0 & \text{if } x \geq L \text{ Reg. III} \end{cases}$$

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* NORMALIZATION + probability interpretation

wave functions



can be multiplied by arbitrary factor without changing ~~meaning~~ quantum-mechanical meaning.

E.g., $\Psi(x)$, $10\Psi(x)$, $(5-8i)\Psi(x)$, $4e^{i\sqrt{2}}\Psi(x)$

Complex # $Ae^{i\theta} \rightarrow \theta$ is the PHASE = $A\cos\theta + i(A\sin\theta)$ $e^{i\theta}$ is a PHASE FACTOR
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all have the same physical content. Best to use Normalized wavefunction:

If $\tilde{\Psi}(x)$ is not normalized, use $\Psi(x) = \frac{\tilde{\Psi}(x)}{\sqrt{N}}$

where ~~N~~ $N = \langle \tilde{\Psi} | \tilde{\Psi} \rangle = \int dx |\tilde{\Psi}(x)|^2$

Then $\langle \Psi | \Psi \rangle = \int dx |\Psi(x)|^2 = \frac{\int dx |\tilde{\Psi}(x)|^2}{N} = 1$

Why? If $\int |\Psi(x)|^2 dx = 1$, then $|\Psi(x)|^2$ can be interpreted as probability density:

$|\Psi(x)|^2 dx$ is the prob^y that pcle is found between x and $x+dx$.

Sum of probabilities should ^(of course) be 1. ~~1~~

For discrete Hilbert space: ~~two~~ ^{rotations:} 42

[a] ~~Express~~ states in terms of basis set

$$\{|\phi_j\rangle\}: |\Psi\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle + c_3|\phi_3\rangle + c_4|\phi_4\rangle$$

~~\{|\phi_j\rangle\}~~ usually taken to be orthonormal!

$$\langle\phi_i|\phi_j\rangle = \delta_{ij} \quad \left. \begin{array}{l} = \text{each normalized} \\ + \text{orthogonal to each other.} \end{array} \right\}$$

If $|\Psi\rangle$ is normalized: $|c_1|^2 + |c_2|^2 + |c_3|^2 + \dots = 1$

If system state is $|\Psi\rangle$, the prob^{ab} to find system ~~having~~ properties of $|\phi_1\rangle$

is $|c_1|^2$. ~~Since~~ $|c_i|^2$ are probabilities,

their sum should be ~~1~~ 1. $\sum |c_i|^2 = 1$

[b] Matrix representation: $|\phi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$, $|\phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$

$$|\phi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, |\phi_4\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

$$|\Psi\rangle = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

Normalization

implies $\sum |c_i|^2 = 1$

Notice similarity to $\int |\psi(x)|^2 dx = 1$
Basis? $\phi(x) = \delta(x)$

* Norm of wavefunction remains unchanged

during time evolution. $i\hbar \frac{\partial \Psi(t)}{\partial t} = \hat{H} \Psi(t)$

If \hat{H} is not itself time-dependent, solution can be formally written as:

$$\Psi(t) = e^{-i\hat{H}t/\hbar} \Psi(0) = \exp\left[-\frac{i}{\hbar} \hat{H} t\right] \Psi(0)$$

~~Matrix exponential~~ Matrix exponential or operator exponential, defined as $e^{\alpha \hat{A}} = \hat{I} + \alpha \hat{A} + \frac{\alpha^2}{2} \hat{A} \hat{A} + \frac{\alpha^3}{6} \hat{A} \hat{A} \hat{A} + \dots$

~~Exponentiating~~ Exponentiating (hermitian operators)^{x_{ij}} gives

Unitary operators. [Def: \hat{U} is unitary if $\hat{U} \hat{U}^\dagger = \hat{U}^\dagger \hat{U} = \mathbb{I}$, i.e., $\hat{U}^\dagger = \hat{U}^{-1}$]

Unitary operations on vectors/states/w.f.'s keep the norm unchanged.

\Rightarrow If $\Psi(0)$ is normalized and so has prob^y interpretation, it will continue to have prob^y interpretation at later time.