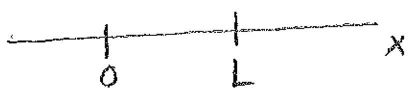
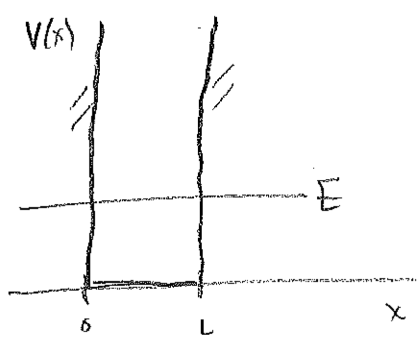
[Bound particles:
electron in hydrogen atom
neutron in a nucleus
conduction electron in metal.
But all of these can get out; become unbound.]

<u>Particle in a box</u> : an absolutely bound particle

$0 < x < L$: allowed region
$V(x) \leq E$

$\left.\begin{array}{l} x < 0 \\ x > L \end{array}\right\}$ forbidden region
$V(x) \geq E$
for any E





$$\text{Let } V(x) = \begin{cases} \infty, & x < 0 \\ 0, & 0 < x < L \\ \infty, & x > L \end{cases}$$

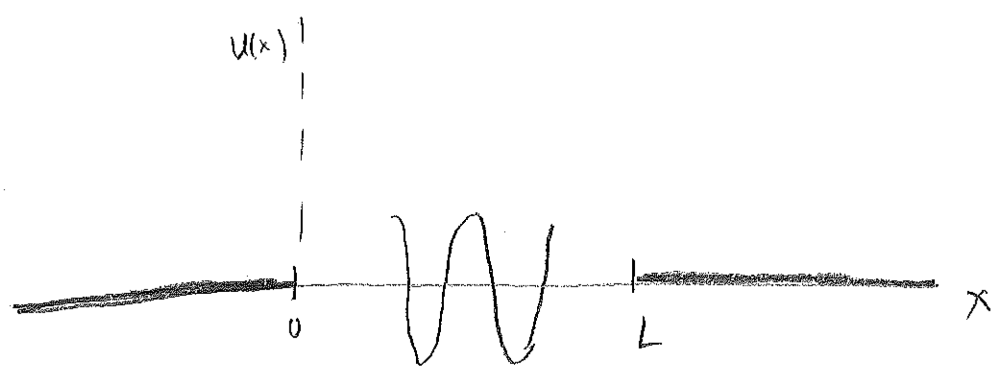
t.i.s.e. $\quad -\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + V(x)\,u = E\,u$

Outside box: $V(x) = \infty \Rightarrow u(x) = 0 \Rightarrow$ Prob density $|u|^2 = 0$

Inside box $V(x) = 0$:

$$\frac{d^2u}{dx^2} = -\frac{2mE}{\hbar^2}\,u$$

$$u = A\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right) + B\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right)$$



[Could use dimensional argument: $\frac{2mE}{\hbar^2}$ has units of (length)$^{-2}$

Define $x = \frac{\hbar}{\sqrt{2mE}}\,y$. $\quad \frac{d^2u}{dy^2} = -u$]

Boundary conditions on solutions of t.i.s.e.

$u(x)$ continuous [doesn't make jumps]

$\frac{du}{dx}$ continuous where $V(x)$ is finite.

$\Rightarrow$ box contains $\frac{n}{2}$ de Broglie wavelengths ($n =$ integer)

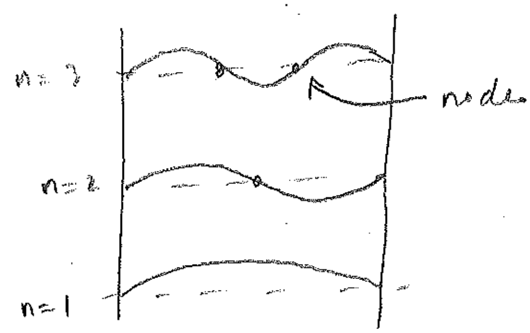
Continuity at $x = 0$: $\quad u(x \to 0_-) = u(x \to 0_+)$

$$0 = A$$

Continuity at $x = L$: $\quad u(x \to L_-) = u(x \to L_+)$

$$B \sin\left(\frac{\sqrt{2mE}}{\hbar} L\right) = 0$$

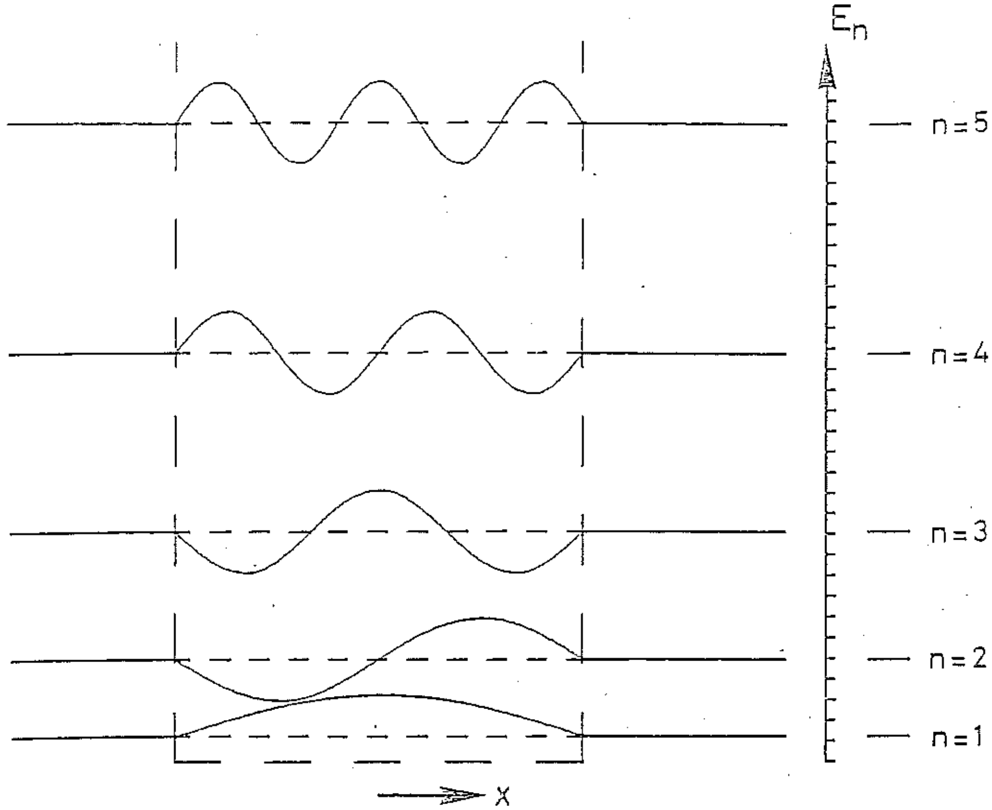
$B \neq 0$ so $\frac{\sqrt{2mE}}{\hbar} L = \pi n \quad \Rightarrow \quad E_n = \left(\frac{\pi^2 \hbar^2}{2mL^2}\right) n^2$

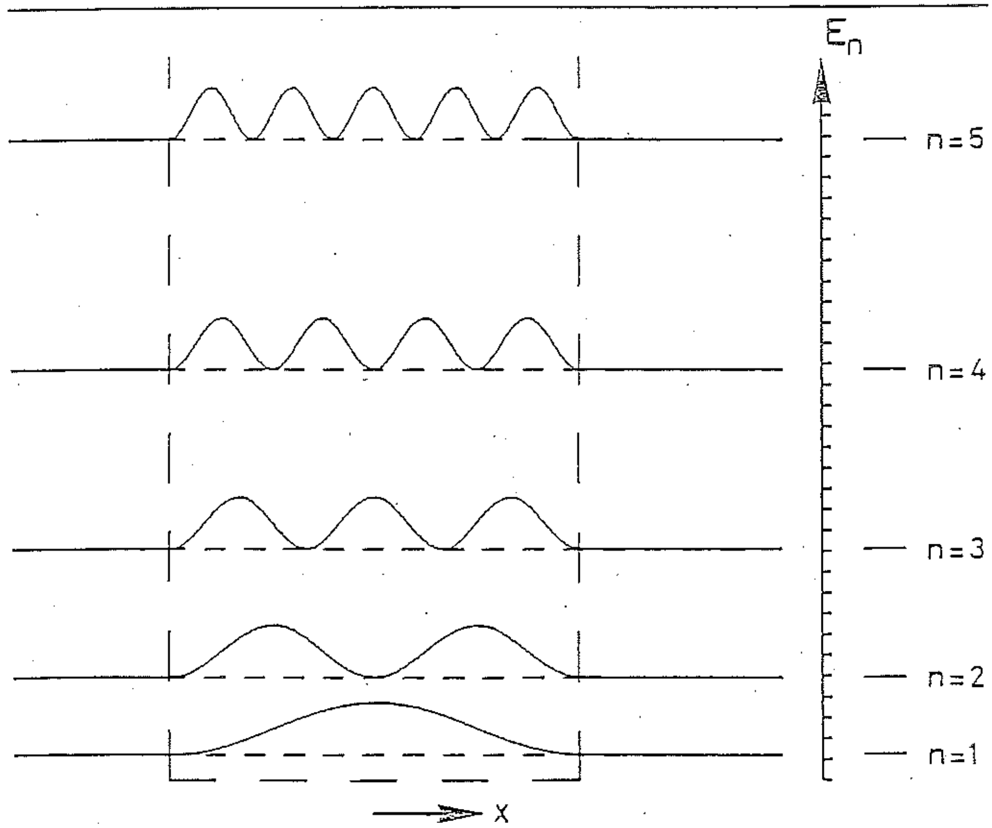


$$u(x) = \begin{cases} 0 & x < 0 \\ B \sin\left(\frac{\pi n x}{L}\right) & 0 < x < L \\ 0 & x > L \end{cases}$$

$n = 0$ not physical
$n < 0$ same as $n > 0$
restrict $n = 1, 2, 3 \ldots$

nodes $= n - 1$
(not incl. boundaries)


E_n
n = 5
n = 4
n = 3
n = 2
n = 1
x


E_n
n = 5
n = 4
n = 3
n = 2
n = 1
x

$$|u(x)|^2 = \begin{cases} |B|^2 \sin^2\left(\frac{\pi n x}{L}\right) & 0 < x < L \\ 0 & \text{outside box} \end{cases}$$

Normalize eigenfunctions

$$1 = \int_{-\infty}^{\infty} |u(x)|^2 dx = |B|^2 \int_0^L \sin^2\left(\frac{\pi n x}{L}\right) dx$$

Let $y = \frac{\pi n x}{L}$

Use $\sin^2 y = \frac{1}{2} - \frac{1}{2}\cos(2y)$

$$= |B|^2 \frac{L}{2}$$

$\Rightarrow |B| = \sqrt{\frac{2}{L}}$ Choose B to be real: $B = \sqrt{\frac{2}{L}}$

normalized energy eigenfunctions $\Bigg\}$ $u_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n x}{L}\right) & 0 < x < L \\ 0 & \text{outside} \end{cases}$

The eigenfunctions are <u>orthonormal</u>, which means

$$\int_{-\infty}^{\infty} u_n^*(x)\, u_m(x)\, dx = \begin{cases} 1 & \text{if } n = m \\ 0 & \text{if } n \neq m \end{cases}$$

[Prove in exercise]

Show that particle in a box eigenfunctions are orthogonal

$$\int_{-\infty}^{\infty} u_n^*(x)\, u_m(x)\, dx = \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) dx$$

$$= \frac{1}{L} \int_0^L \left[\cos\left(\frac{(m-n)\pi x}{L}\right) - \cos\left(\frac{(m+n)\pi x}{L}\right) \right] dx$$

$$= \frac{1}{\pi} \left[\frac{1}{(m-n)} \sin\left(\frac{(m-n)\pi x}{L}\right) - \frac{1}{(m+n)} \sin\left(\frac{(m+n)\pi x}{L}\right) \right] \Big|_0^L$$

$$= 0 \quad (\text{unless } m = n)$$

PROBLEM 14: Consider a particle in a box. Evaluate (numerically to four significant figures) the probability of finding the particle in the middle third of the box for $n = 1, 2, 3$ and 1000.

As we found in class, a particle in a box of width L has probability density

$$P_n(x) = \frac{2}{L}\sin^2\left(\frac{\pi n x}{L}\right), \qquad \text{for} \qquad 0 < x < L$$

and zero outside the box, where n is the quantum number of the energy eigenfunction. The probability of finding the particle in the middle third of the box is therefore

$$P_n = \frac{2}{L}\int_{L/3}^{2L/3} \sin^2\left(\frac{\pi n x}{L}\right)\, dx = \frac{2}{\pi n}\int_{\pi n/3}^{2\pi n/3} \sin^2 y\, dy.$$

where $y = (n\pi/L)x$. Calculating this integral as we did in class, one finds

$$P_n = \frac{2}{\pi n}\left[\frac{1}{2}y - \frac{1}{4}\sin(2y)\right]\Bigg|_{\pi n/3}^{2\pi n/3} = \frac{1}{3} - \frac{1}{2\pi n}\left[\sin\left(\frac{4\pi n}{3}\right) - \sin\left(\frac{2\pi n}{3}\right)\right].$$

For specific values of n, we find

$$P_1 = 0.6090, \qquad P_2 = 0.1955, \qquad P_3 = 0.3333, \qquad P_{1000} = 0.3336.$$

−1 each wrong answer (unless stem from same mistake)

As $n \to \infty$, P_n approaches the classical result $P_{\text{cl}} = \frac{1}{3}$.

→ discuss in class:

- Correspondence principle: as $n \to \infty$ quantum → classical
- classically $P = \frac{1}{3}$
- only $P(x)$, not $\Psi(x)$, defined classically

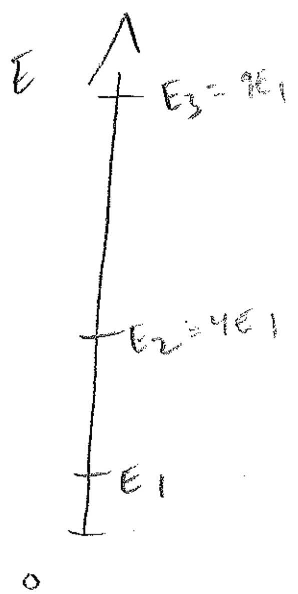
energy eigenvalues for particle in a box

$\Rightarrow$ rederive using $\hat{H}\psi_n = E_n \psi_n$

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2} \quad \text{(ground state)}$$

$$E_n = E_1 n^2$$



Note:

- energy quantization (characteristic of bound particles)

  ↑ confined to a finite region of space

- energy ↑ as # nodes ↑

- lowest possible energy (ground state) is <u>non zero</u> and ↑ as box gets smaller

  "confinement energy"

Exercise

(a) Compute the difference in energy $\delta E = E_{n+1} - E_n$ between 2 successive eigenvalues of a particle in a one dimensional box, and express these in terms of E_n and n

$$E_n = E_1 n^2$$
$$E_{n+1} = E_1 (n+1)^2$$
$$\delta E = E_1 (2n+1) = E_n \left(\frac{2n+1}{n^2}\right) \approx \frac{2E_n}{n}$$

(b) Consider a racketball bouncing around a racquetball court as being in an eigenstate of a particle in a box.
Making plausible estimates for its speed, mass, etc.

$m = 0.04$ kg

$L = 20$ feet $= 6$ m

$v = \frac{7m}{s}$ $\left(\begin{matrix}60 \text{ mph} \\ = 28 \text{ mps}\end{matrix}\right)$

estimate its quantum # no.

$E = \frac{1}{2}mv^2$ $(=11J)$

$= 1 J$

$E_1 = \frac{\hbar^2\pi^2}{2mL^2}$

$= 3E-68 J$

$n = 6\times10^{33}$

(In fact, an actual racquetball would not be described by such a stationary state)

(c) How much more energy would it have if it were in state of qu no $n+1$?

(d) Is energy quantization very noticeable for a macroscopic particle in a box?

(d) What is minimum energy?

Talk about correspondence principle: qu. mech reduces to cl. mech in limit of large quantum numbers

P(x) 

[After presentation of exercise showing orthogonality of box eig. fcns]

Proof that energy eigenfunctions of different energies are orthogonal (provided $u_n(x) \xrightarrow[x \to \pm\infty]{} 0$)

Consider the expression

$$I = \int_{-\infty}^{\infty} \left[(u_n^* \hat{H} u_m) - (u_m^* \hat{H} u_n)^* \right] dx$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x). \quad \text{Since } V^*(x) = V(x)$$

$(u_m^* V u_n)^* = u_m V u_n^*$ so potential cancels out

$$I = -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} \left[u_n^* \frac{d^2 u_m}{dx^2} - u_m \frac{d^2 u_n^*}{dx^2} \right] dx$$

Integrate by parts, and use $u \xrightarrow[x \to \pm\infty]{} 0$

$$I = -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} \left[-\frac{du_n^*}{dx}\frac{du_m}{dx} + \frac{du_m}{dx}\frac{du_n^*}{dx} \right] dx$$

$= 0 \Rightarrow$ expression vanishes

Now evaluate I using $\hat{H} u_n = E_n u_n$

$$I = \int_{-\infty}^{\infty} \left[u_n^* E_m u_m - \underbrace{(u_m^* E_n u_n)^*}_{u_m E_n u_n^*} \right] dx \quad \text{because } E_n^* = E_n$$

$$= (E_m - E_n)\int_{-\infty}^{\infty} u_n^* u_m \, dx$$

$\Rightarrow$ either $E_m - E_n = 0$ or $\int_{-\infty}^{\infty} u_n^* u_m \, dx = 0$

but energies are different so eigenfunctions are orthogonal!