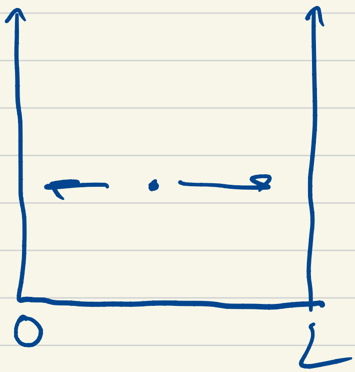
Lecture 6 - Particle-in-a-box

Apply QM model to very simple system.

$$V(x) = \begin{cases} 0, & 0 < x < L \\ \infty, & x \leq 0, x \geq L \end{cases}$$



Schrödinger eq

$$\left\{ -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \cancelto{0}{V(x)} \right\} \psi(x) = E\psi(x)$$

Boundary conditions $\psi(0) = \psi(L) = 0$

∞ potential $\rightarrow$ impenetrable

$$-\frac{d^2}{dx^2}\psi(x) = \frac{2mE}{\hbar^2}\psi(x)$$

$$\psi(x) = c_1 \sin kx + c_2 \cos kx$$

$$\psi'(x) = c_1 k \cos kx - c_2 k \sin kx$$

$$\psi''(x) = -c_1 k^2 \sin kx - c_2 k^2 \cos kx$$

$$= -k^2 \cdot \psi(x)$$

$$k^2 = \frac{2mE}{\hbar^2} \quad , \quad E = \frac{\hbar^2 k^2}{2m}$$

Boundary conditions

$$\psi(0) = c_1 \sin(0) + \cancelto{0}{c_2} \cancelto{1}{\cos(0)} = 0$$

$$\psi(x) = c_1 \sin kx$$

$$\psi(L) = c_1 \sin kL = 0 \rightarrow kL = n\pi$$

$$n = 1, 2, 3, \cdots$$

$$k = \frac{n\pi}{L}$$

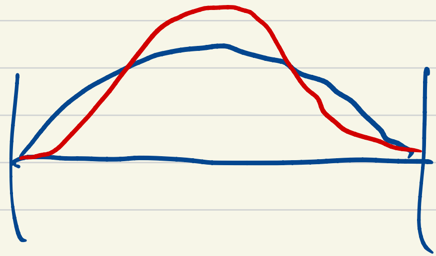
$$\psi_n(x) = c_1 \sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

standing waves

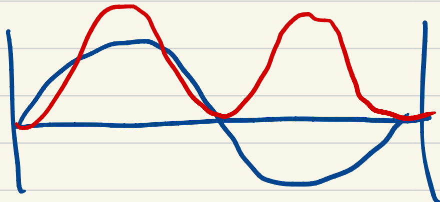
$$\lambda = \frac{2\pi}{k} = \frac{2L}{n} \quad , \quad \lambda = 2L, L, \frac{2L}{3}, \ldots$$

$n \uparrow \quad \lambda \downarrow \quad$ nodes $\uparrow \quad E \uparrow$

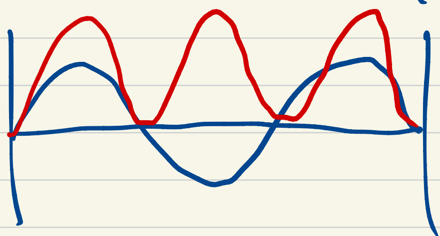
$n=1 \quad E_1 \quad 2L$



$n=2 \quad 4E_1 \quad L$



$n=3 \quad 9E_1 \quad \frac{2}{3}L$



normalize

$$\langle \psi_n | \psi_n \rangle = c_1^2 \int_0^L \sin^2 \frac{n\pi x}{L}\, dx$$

$$= c_1^2 \frac{L}{2} = 1$$

$$\Rightarrow c_1 = \pm\sqrt{\frac{2}{L}}$$

orthonormal?

$0 \quad n \neq m$

$$\langle \psi_m | \psi_n \rangle = \frac{2}{L} \int_0^L \sin \frac{n\pi x}{L} \sin \frac{m\pi x}{L}\, dx$$

Wilson Ho paper

position & momentum

$$\hat{p}_x \psi(x) \not\propto \psi(x)$$

$$p = \sqrt{2mE} = \pm n \frac{\pi \hbar}{L}$$

$$\psi(x) = \frac{e^{+in\pi\hbar/L} + e^{-in\pi\hbar L}}{2}$$

superposition

$\hat{x}\, \psi(x) \not\propto \psi(x)$ } neither precise position or momentum known

$$\Delta x \sim L \Rightarrow \Delta p_x \sim \hbar/2L$$

By uncertainty principle, confined particle must have momentum and thus a kinetic energy!

Zero point energy

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \neq 0 \; !!$$

example

	car	e^-
m	1000 kg	9.1×10^{-31} kg
L	10 m	10^{-9} m
E_1	5×10^{-76} J	6×10^{-20} J
	$\sim10^{-52}$ kJ/mol	0.38 eV
		! $\sim$ 40 kJ/mol

Illustrates correspondence principal
QM behaviour dissolves into classical
behavior @ large sizes.

$k_BT \sim 0.026\,\text{eV}$ @ 298 K

$N_{car} \sim 3\times10^{27}$ $\quad N_{e^-} \sim 4$

To center box, apply $u = x - \frac{L}{2}$

$$-\frac{L}{2} < u < \frac{L}{2}$$

$$x = u + L/2$$

$$\sin\frac{n\pi x}{L} \rightarrow \sin\left\{\left(\frac{n\pi}{L}\right)\left(u + \frac{L}{2}\right)\right\}$$

$$\rightarrow \sin\frac{n\pi u}{L}\cos\left(\frac{n\pi}{2}\right) + \cos\frac{n\pi u}{L}\sin\left(\frac{n\pi}{2}\right)$$

$n = 1 \qquad \psi_1 = \cos\frac{\pi u}{L}$

$n = 2 \qquad \psi_2 = -\sin\frac{2\pi u}{L}$

$n = 3 \qquad \psi_3 = -\cos\frac{3\pi u}{L}$

...

- - - - - - - - - - - - - - - - -

-or- $\psi = c_1 e^{iku/L} + c_2 e^{-iku/L}$

$n=1 \qquad k = \pi \qquad c_1 = -c_2$

$n=2 \qquad k = 2\pi \qquad c_1 = c_2$

...

Multiple dimensions

Suppose box is cubic.

$$V(x,y,z) = \begin{cases} 0, & |x|,|y|,|z| < \frac{L}{2} \\ \infty, & |x| \text{ or } |y| \\ & \text{or } |z| \geq \frac{L}{2} \end{cases}$$

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + \xcancel{V(x,y,z)}^{\,0}\right\}\psi(x,y,z) = E\,\psi(x,y,z)$$

ψ vanishes outside box

Separate variables $\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$

substitute & divide by XYZ

$$-\frac{\hbar^2}{2m}\left\{\underbrace{\frac{1}{X}\frac{d^2}{dx^2}X}_{E_x} + \underbrace{\frac{1}{Y}\frac{d^2}{dy^2}Y}_{E_y} + \underbrace{\frac{1}{Z}\frac{d^2}{dz^2}Z}_{E_z}\right\} = E$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X(x) = E_x X(x) \qquad \& \; y \; \& \; z$$

identical to 1D problem...

$$X_l(x) = \sqrt{\frac{2}{L}} \sin \frac{l\pi x}{L} \qquad E_x = \frac{l^2 \pi^2 \hbar^2}{2mL^2}$$

$$\Psi_{lmn}(x,y,z) = X_l(x)\, Y_m(y)\, Z_n(z)$$

$$E = \frac{(l^2+m^2+n^2)\, \hbar^2 \pi^2}{2mL^2}$$

		nodes	shape
$12E_0$	(2,2,2)	3	f
$11E_0$	(3,1,1) (1,3,1) (1,1,3)	2	"d"
$9E_0$	(2,2,1) (2,1,2) (1,2,2)	2	d
$6E_0$	(2,1,1) (1,2,1) (1,1,2)	1	p
$3E_0$	(1,1,1)	0	s

See python notebook

each dimension → new Q.N.
→ nodes

symmetry of problem leads to
degenerate solutions

"degeneracy"

3d box states look like... an atom!

- - - - - - - - - - - - - - -

independent e^- approximation

add e^- from bottom-up

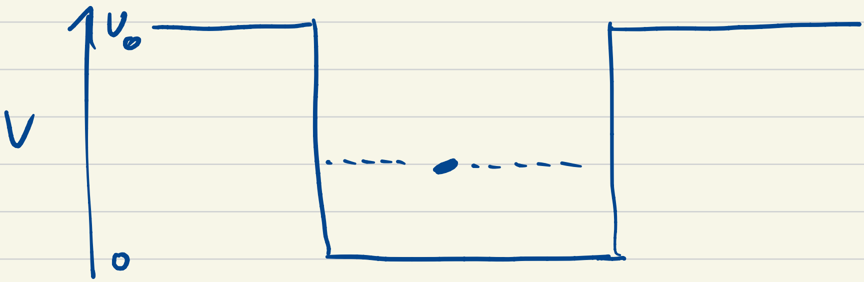
e^- have "spin": ↑ + ↓

add 2/energy level

qualitatively useful, neglects
$e^- - e^-$ interactions.

Will improve later.

finite depth well



Classically, 2 possibilities:

$E < V_0$, bounce between walls

$E > V_0$, fly right past well

QM? Boundary conditions change

If $E < V_0$, have $\lim_{x \to \pm\infty} \psi(x) = 0$

(bound state)

In well region ("classical" region)

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

$$\psi \sim \sin kx \sim e^{ikx} - e^{-ikx}, \quad k = \sqrt{\frac{2mE}{\hbar}}$$

> 0

Outside well

$$\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + V_0\psi\right\} = E\psi$$

$$\frac{d^2}{dx^2}\psi = \underbrace{-\frac{2m(E-V_0)}{\hbar^2}}_{>0}\psi$$

$$\frac{d^2}{dx^2}\psi = \kappa^2\psi \qquad \kappa = \frac{\sqrt{2m(V_0-E)}}{\hbar}$$

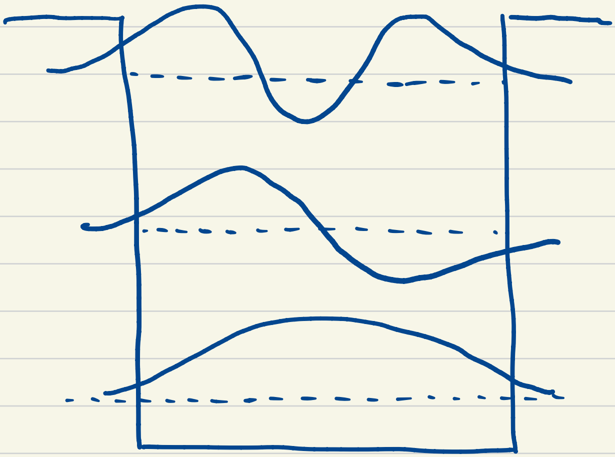
$$\Rightarrow \quad \psi \sim e^{\kappa x} + e^{-\kappa x}$$

$\neq 0$!!

exponential decay in "forbidden" region

To solve exactly, would have to require wavefunction & derivatives to match @ boundaries.

would be nice to write this code!!



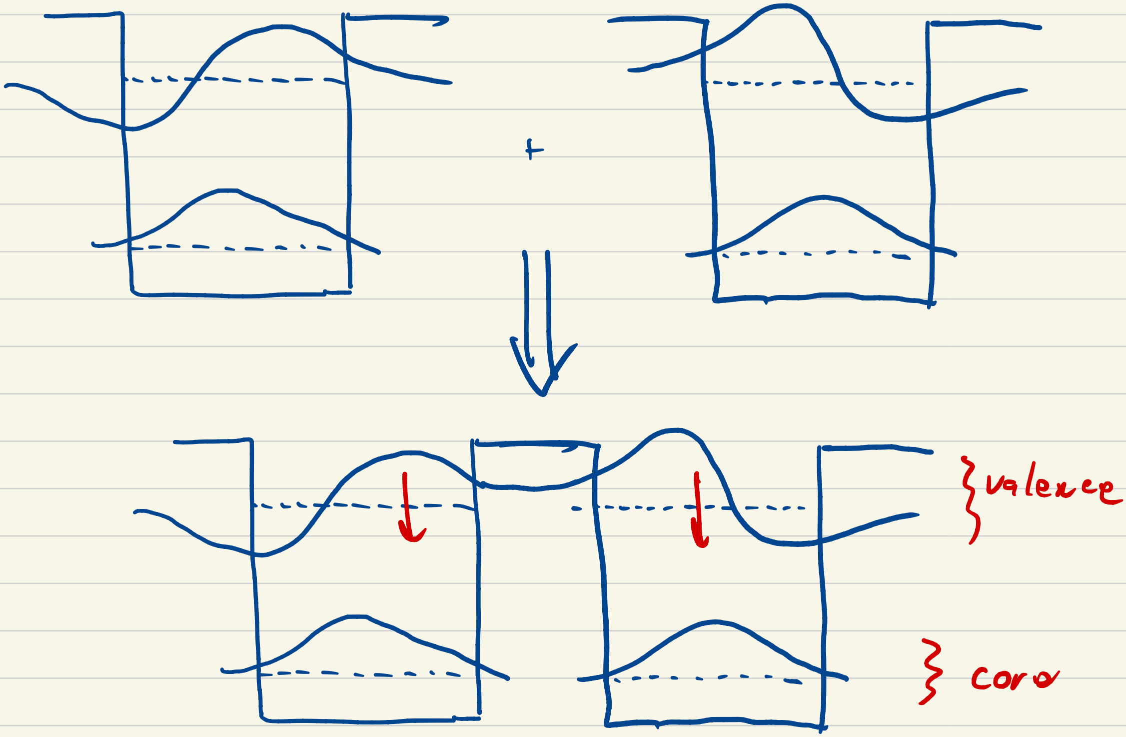
$V_0 - E$ small
κ small
decay slow

$V_0 - E$ big
κ big
decay fast

- probability to explore "forbidden" region $\neq 0$
- probability ↑ as $V_0 - E$ ↓
- energy of states ↓ relative to infinite well

  explore more space → KE ↓ *
- retain nodal structure
- finite number of bound states.

Better representation of an atom ...



"overlap", or constructive interference, through barrier expands region explored be e^- and lowers energy

That's a chemical bond

$$E_{A-B} < E_A + E_B$$

Only works for wavefunctions that sneak out of well ("valence") and that match each other energetically

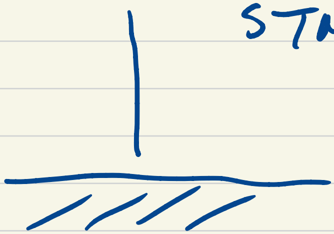
"homonuclear" bond.

contrast "heteronuclear"

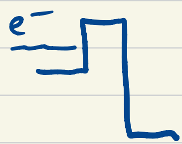
Chemical bonding is one hugely important! example of QM tunnelling

Other examples involving e^-

STM



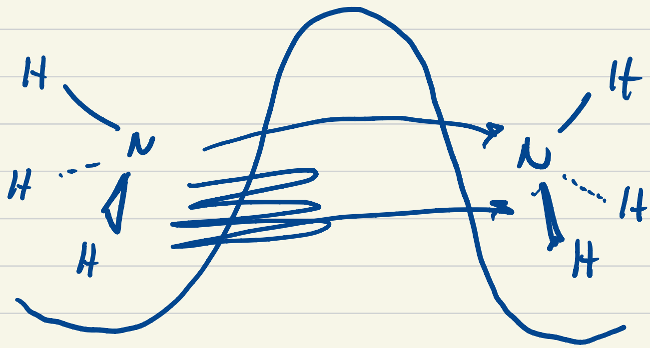
"tunneling diode"



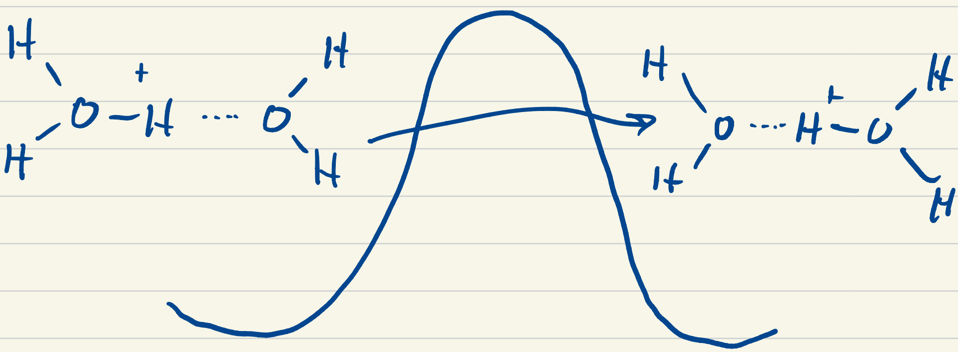
$\kappa \propto m^{1/2}$ → probability to tunnel ↓ as m ↑

Only other particle for which tunneling is practically important in a proton

eg



or



will vibrate in one well, occassionally "appear" on other side!!