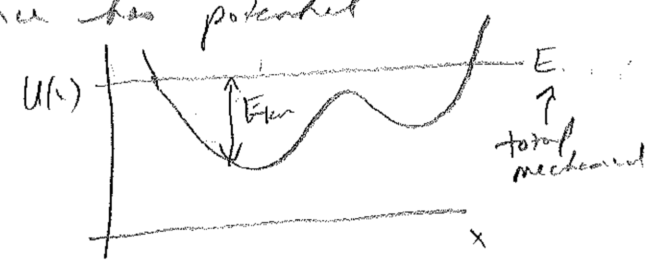
Recall

A free electron is described by a travelling wave

$$\psi = A\cos(kx-\omega t) + i\,A\sin(kx-\omega t)$$

where $k = \frac{2\pi}{\lambda}$ and $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_{kin}}} \Rightarrow E_{kin} = \frac{h^2}{2m\lambda^2}$

An electron experiencing a force has potential as well as kinetic energy



It is described by a wave ψ satisfying the Schrödinger equation (1926)

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi = E\psi}$$

valid for a particle with well-defined energy

Let's check this for a free electron

A free electron experiences no force, so its potential energy vanishes. $U(x) = 0$, and $E_{mech} = E_{kin}$

Schrödinger eqn is:

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

$$\psi = A\cos(kx - \omega t) + iA\sin(kx - \omega t)$$

$$\frac{d\psi}{dx} = -Ak\sin(kx - \omega t) + iAk\cos(kx - \omega t)$$

$$\frac{d^2\psi}{dx^2} = -Ak^2\cos(kx - \omega t) - iAk^2\sin(kx - \omega t)$$

$$= -k^2\psi$$

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

$$= \frac{\hbar\left(\frac{2\pi}{\lambda}\right)^2}{2m}\psi$$

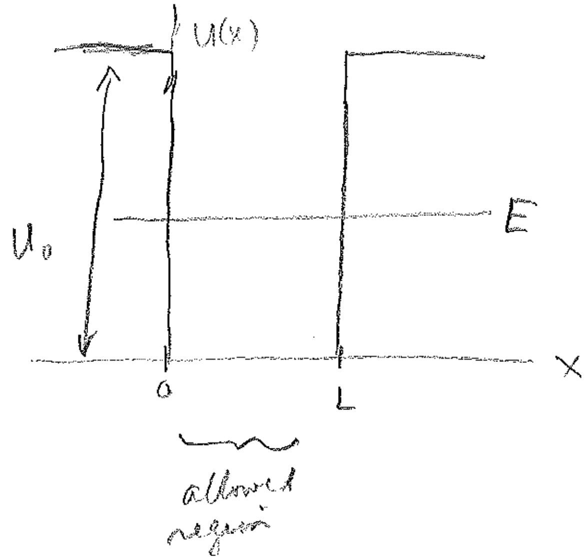
$$= \frac{(2\pi\hbar)^2}{2m\lambda^2}\psi$$

$$= \frac{h^2}{2m\lambda^2}\psi$$

$$= E_{kin}\psi$$ so ψ does satisfy Schrödinger eqn

Consider a "particle in a box" of width L:
an electron confined to a region $0 < x < L$
by a strong force

Potential energy $U(x) = \begin{cases} 0 & 0 < x < L \\ U_0 & \text{outside the box} \end{cases}$



Schrodinger eqn inside the box is same as for a free electron

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

and has the solution $\psi = N \sin kx$ [purely real]

$$\frac{d^2\psi}{dx^2} = -k^2 N \sin kx = -k^2\psi$$

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

energy of the electron $E = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$

λ is determined by the boundary conditions

If the potential energy outside the box is infinite ($U_0 \to \infty$) there is zero probability that the electron is outside

$\Rightarrow \psi = 0$ for $x < 0$ and $x > L$.

Require the wavefunction to be continuous at the boundaries

$$\psi = \begin{cases} 0, & x < 0 \\ N \sin kx, & 0 < x < L \\ 0, & x > L \end{cases}$$

ψ is automatically continuous at $x = 0$ since $\sin(0) = 0$

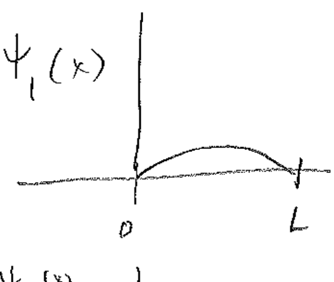
ψ is continuous at $x = L$ if $\sin kL = 0$

$\Rightarrow kL = n\pi$ for some integer n

Define $k_n = \frac{n\pi}{L}$ $\Rightarrow \lambda_n = \frac{2\pi}{k_n} = \frac{2L}{n}$ ← quantized de Broglie wavelength

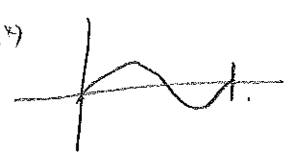
$$\psi_n(x) = N \sin(k_n x) = N \sin\left(\frac{n\pi x}{L}\right)$$

$\psi_1(x)$



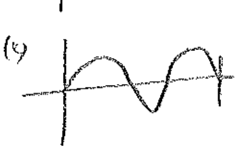
$\lambda_1 = 2L$

$\psi_2(x)$



$\lambda_2 = L$

$\psi_3(x)$



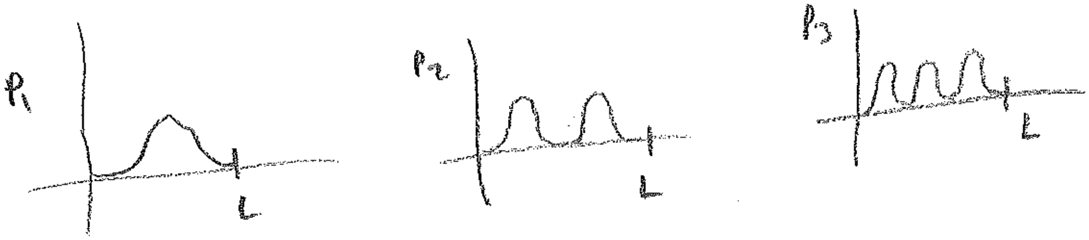
$\lambda_3 = \frac{3L}{2}$

⋮

Probability density $\rho(x) \equiv |\psi(x)|^2 = \psi_R^2 + \psi_I^2$

For particle in a box, ψ is purely real so $\rho(x) = \psi_R^2$

$$P_n(x) = \begin{cases} N^2 \sin^2\left(\frac{n\pi x}{L}\right), & \text{inside box} \\ 0 & \text{, outside} \end{cases}$$



$\rho(x)dx$ = prob. of finding particle between x and $x+dx$

$\int_a^b \rho(x)dx$ = prob. of finding particle between $x=a$ and $x=b$

$\int_{-\infty}^{\infty} \rho(x)dx$ = prob of finding particle anywhere $= 1$

$$\Rightarrow \boxed{\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1}$$ normalization condition

For particle in a box

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

use this to find the value of N

[problem]

$$E = \frac{h^2}{2m\lambda^2} = \frac{h^2}{2m}\left(\frac{n}{2L}\right)^2 = \left(\frac{h^2}{8mL^2}\right)n^2$$

Energy of electron increases w/ n

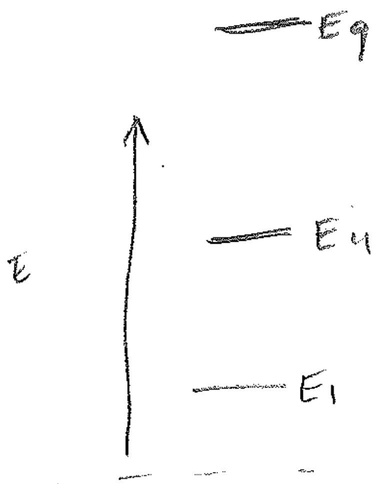
$$E_n = \frac{\hbar^2 k_n^2}{2m} = \left(\frac{\hbar^2 \pi^2}{2mL^2}\right) n^2$$

$$n = 1 \Rightarrow E_1 = \frac{\hbar^2 \pi^2}{2mL^2} \quad \text{(ground state)}$$

$$E_n = E_1 n^2$$

$n = 2 \qquad E_2 = 4E_1$ (1st excited state)

$n = 3 \qquad E_3 = 9E_1$ (2nd excited state)

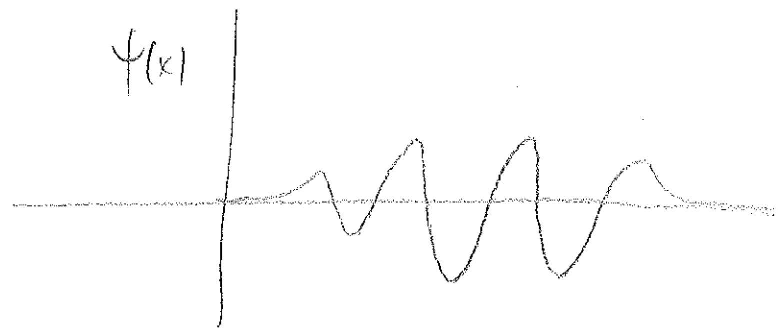


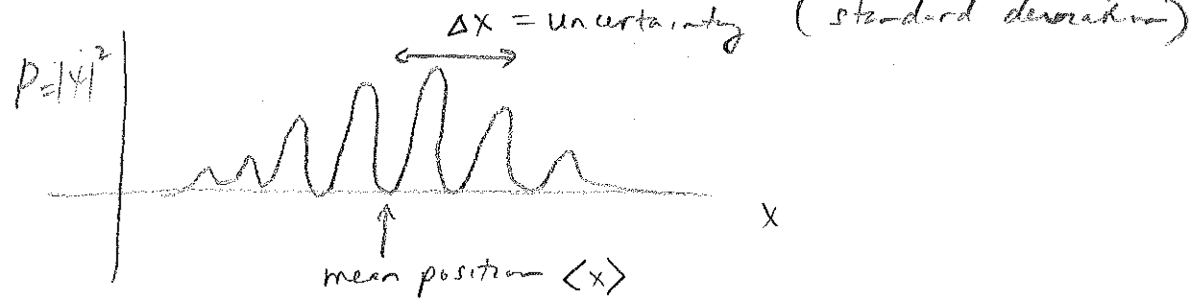
analogous to hydrogen atom;
also electrons in a metal

$n = 0$ not possible because $\psi = 0 \Rightarrow$ no particle
$n < 0$ do not give separate solutions

When electron transitions from one energy level to another, it emits a photon whose energy is the difference between the energy levels

The position of particle is not necessarily well-defined





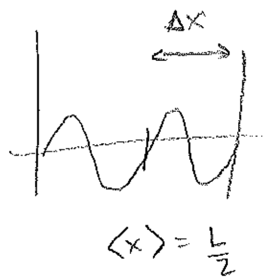
The momentum of a particle is also not necessarily well-defined (if not monochromatic)

Δp = uncertainty in momentum

Heisenberg established the uncertainty principle which holds for all particles

$$\Delta p \, \Delta x \geq \frac{\hbar}{2}$$

[Let's see how this works for particle in a box]



$\Delta x \sim \frac{L}{2}$

$$p = \frac{h}{\lambda} = \frac{hn}{2L} = \frac{\pi \hbar n}{L}$$

But can move left or right $\Rightarrow$ $p_x = \pm p$

$$\Delta p \simeq \frac{p - (-p)}{2} = p = \frac{\pi \hbar n}{L}$$

As $L \downarrow$, $\Delta x \downarrow$ but $\Delta p \uparrow$ so

product remains const

$$\Delta p \, \Delta x \sim \frac{\pi \hbar n}{2}$$

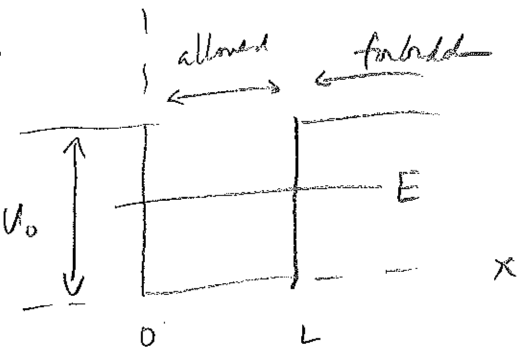
uncertainty relation satisfied

Since $n\pi > 1$, $\Delta p \, \Delta x \geqslant \frac{\hbar}{2}$

for $n \geqslant 1$

Consider a finite potential well

$$U(x) = \begin{cases} U_0 & x<0 \\ 0 & 0<x<L \\ U_0 & x>L \end{cases}$$



Schrödinger $\quad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi = E\psi$

Inside the well $U(x)=0 \Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$

has solution $\quad \psi = N_1 \sin kx + N_2 \cos kx \quad$ w/ $E = \frac{\hbar^2 k^2}{2m}$

Outside the well $U(x) = U_0 \Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E-U_0)\psi$

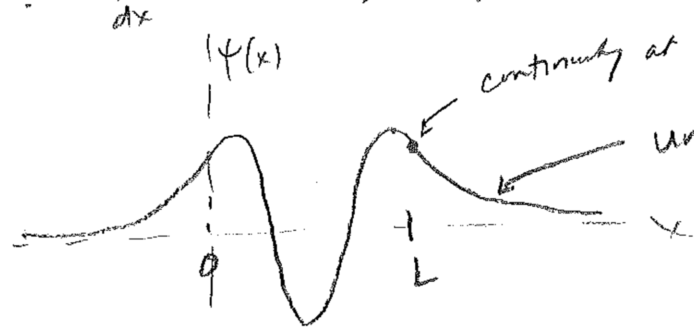
$$\frac{d^2\psi}{dx^2} = \underbrace{\frac{2m}{\hbar^2}(U_0 - E)}_{\text{positive number, call it } \alpha^2}\psi$$

$$\Rightarrow \frac{d^2\psi}{dx^2} = \alpha^2\psi$$

Solution is not $\sin kx$ or $\cos kx$. Instead

$$\psi = e^{+\alpha x} \text{ or } e^{-\alpha x}$$

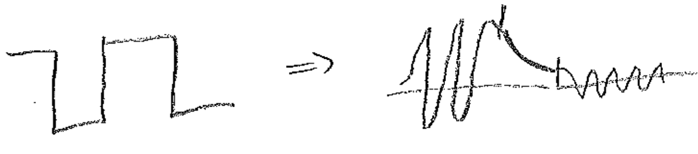
check: $\frac{d\psi}{dx} = \alpha e^{\alpha x}, \quad \frac{d^2\psi}{dx^2} = \alpha^2 e^{\alpha x} = \alpha^2\psi \quad \checkmark$



continuity at boundary

unlikely but possible to find particle in forbidden region

Talk about tunnelling:



- scanning tunnelling microscope
- radioactive decay