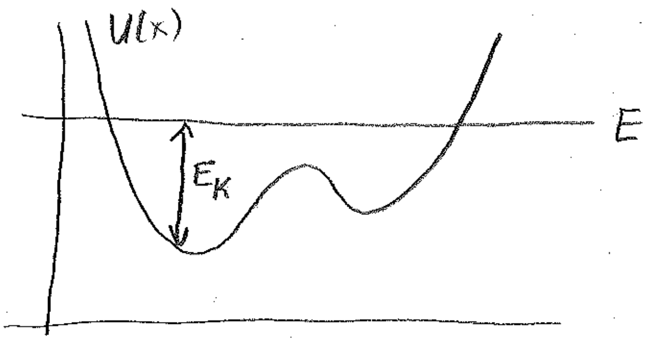
Schrödinger equation

An electron experiencing a force
(e.g. due to the proton in a hydrogen atom,
or due to the conductor in which it is confined)
has potential energy U as well as kinetic energy E_K



Total mechanical energy is $E = E_K + U = \text{constant}$

The matter wave ψ describing the electron
obeys the Schrödinger equation

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

valid for an electron with well-defined energy

Let's check that free electron obeys Schrödinger eqn.

Free electron is described by a travelling matter wave

$$\psi = A\cos(kx-\omega t) + iA\sin(kx-\omega t) \qquad \text{where } k = \frac{2\pi}{\lambda}$$

$$\text{and } \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_k}} \implies E_k = \frac{h^2}{2m\lambda^2}$$

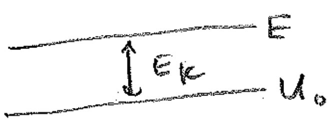
Take derivatives

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

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

$$= -k^2\psi$$

A free electron experiences no force, so $U = U_0 = \text{const}$



L.h.s of Schrödinger eqn

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U\psi = \frac{\hbar^2k^2}{2m}\psi + U_0\psi = (E_k + U_0)\psi = E\psi$$

$$\text{But } \frac{\hbar^2k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{\lambda}\right)^2 = \frac{(2\pi\hbar)^2}{2m\lambda^2} = \frac{h^2}{2m\lambda^2} = E_k$$

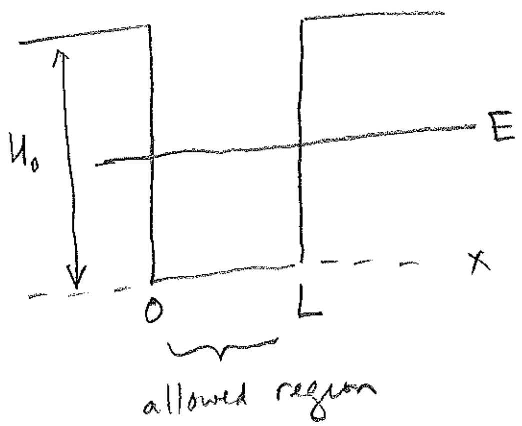
r.h.s of Schrödinger eqn

Particle in a box

Electron is confined to a region $0<x<L$
by a strong force (eg. conduction electrons in a metal)

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

U_0 ← very large



Schrodinger eqn inside box ($U=0$) is

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

Verify that it has solution (similar to free electron)

$$\psi = N\sin(kx) \quad \leftarrow \text{purely real}$$

$$\frac{d\psi}{dx} = Nk\cos(kx)$$

$$\frac{d^2\psi}{dx^2} = -Nk^2\sin(kx) = -k^2\psi$$

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

As before $E = \dfrac{h^2}{2m\lambda^2}$ but what is λ?
Determined by boundary conditions.

If confining force is very strong, $U_0 \to \infty$ outside box and there is zero probability to find electron there

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

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

We require that ψ be continuous at the boundaries

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

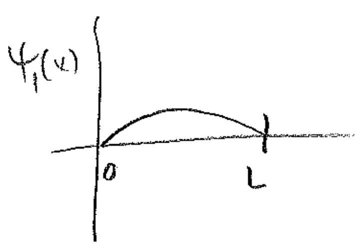
ψ is continuous at $x = L$ if $N \sin(kL) = 0$

only possible if $kL = n\pi$ for some integer n

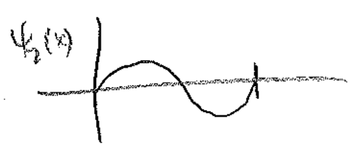
Define $k_n = \frac{n\pi}{L}$ $\Rightarrow$ $\lambda_n = \frac{2\pi}{k_n} = \frac{2L}{n}$

De Broglie wavelength is quantized inside the box

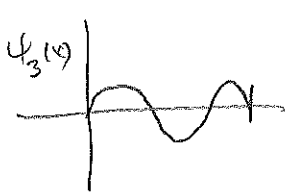
$$\psi_n(x) = N \sin(k_n x) = N \sin\left(\frac{n\pi x}{L}\right)$$



$\lambda_1 = 2L$



$\lambda_2 = L$

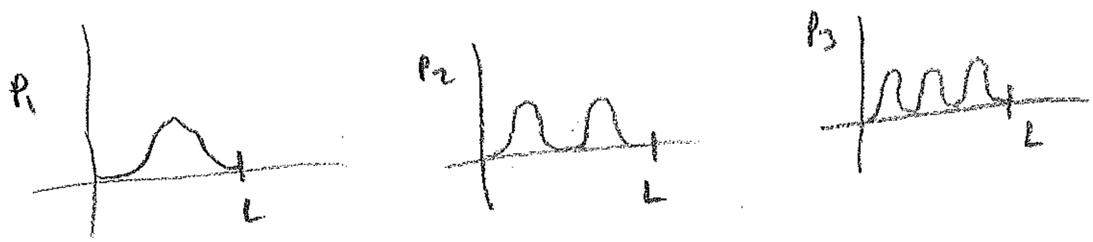


$\lambda_3 = \frac{2L}{3}$

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

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

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



$\rho(x)dx$ = 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

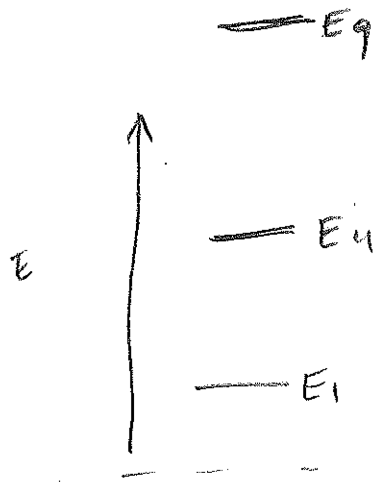
$$E_n = \frac{\hbar^2 k_n^2}{2m} = \left(\frac{\hbar^2\pi^2}{2mL^2}\right)n^2$$

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

$$E_n = E_1 n^2$$

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

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



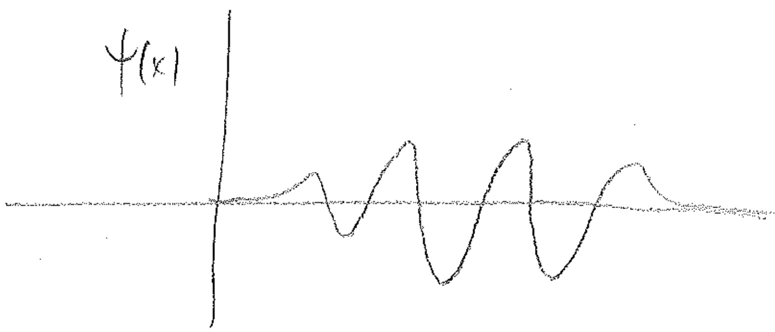
analogous to hydrogen atom; also electrons in a metal

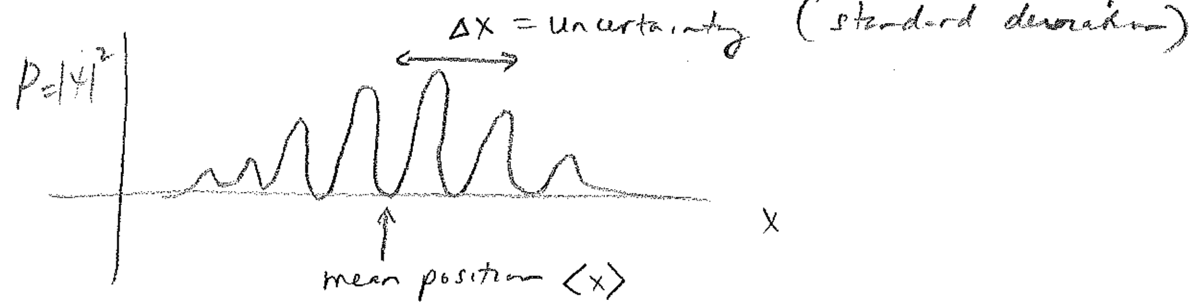
$n = 0$ not possible because $\psi = 0 \Rightarrow$ no particle

$n < 0$ 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





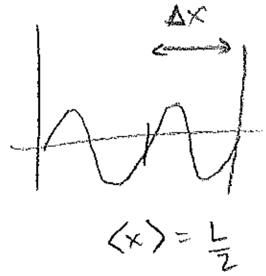
The momentum of a particle is also not necessarily well-defined (if not monochromatic)

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 $\Rightarrow$ $p_x = \pm p$

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

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

product remains const

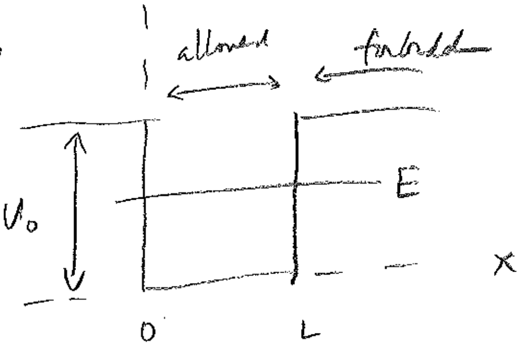
$$\Delta p\, \Delta x \sim \frac{\pi\hbar n}{2}$$

uncertainty relation satisfied

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

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

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

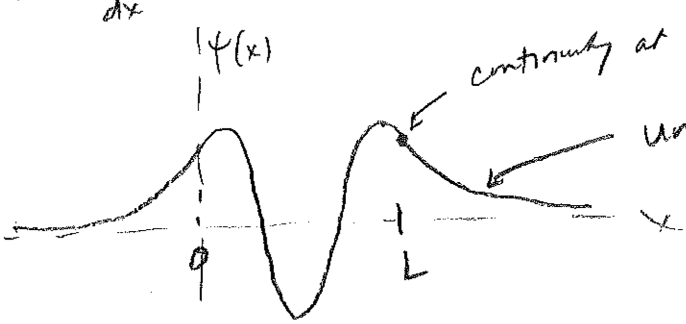
$$\frac{d^2\psi}{dx^2}=\underbrace{\frac{2m}{\hbar^2}(U_0-E)}_{\text{positive number, call it } \alpha^2}\psi$$

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

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

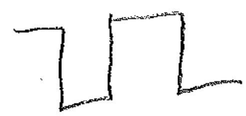
$$\psi = e^{+\alpha x} \text{ or } e^{-\alpha x}$$

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



continuity at boundary

unlikely but possible to find particle in forbidden region

Talk about tunnelling:  $\Rightarrow$ 

- Scanning tunnelling microscope
- radioactive decay