Quantum Mechanical Wave Eqn

- Quick recap:

A free particle moving → $+x$ has wavefn

$$\psi = Ae^{ikx} e^{-i\omega t}$$

Time- and position dependence can be factorised / separated

Schrödinger

- To build the Schrödinger Equation (wave eqn for a QM free particle in a potential $V(x,t)$:

  - Assumptions:

    ⇒ Energy conservation $T + V = E$

    ⇒ Linear diff. eqn. so superposition of waves still works

so $\psi, \frac{\partial \psi}{\partial t}, 2\frac{\partial^2 \psi}{\partial x^2} \ldots$ ✓ OK terms

and $\frac{1}{\psi}, \left(\frac{\partial \psi}{\partial x}\right)^2, \sin\frac{\partial^2 \psi}{\partial x^2} \ldots$ ✗ not OK

⇒ Must be consistent with:

$$p = \frac{h}{\lambda} = \hbar k \quad , \quad E = hf = \hbar\omega$$

from before

['$\hbar$' ?? "h bar" is just $\frac{h}{2\pi}$

$\hbar = 1.0546 \times 10^{-34}$ Js]

- Now the game is to guess what terms to tell us kinetic energy, total energy etc might look like then throw them into $T + V = E$

→ $\Psi = Ae^{ikx} e^{-i\omega t}$ has k and ω in it → info on p, E is in there!

→ Let's try $\frac{\partial}{\partial x}$:

$$\frac{\partial}{\partial x}\Psi(x,t) = ikAe^{ikx}e^{-i\omega t}$$

$$= ik\Psi$$

interesting! so how about...

$$-i\hbar\frac{\partial}{\partial x}\Psi = -i\hbar ik\Psi = \underbrace{\hbar k}_{p\text{, momentum!}}\Psi$$

→ OK, identify $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

as the momentum operator in the x direction

We can then write this eigenvalue equation

unchanged wavefn

$$\hat{p}_x \Psi = p_x \Psi$$

Operator   Real number (eigenvalue)

[Note that this is like matrix maths, operators do not commute: $\hat{p}_x \Psi \neq \Psi \hat{p}_x$]

[Note also - the fact that this works, and we get an eigenvalue tells us momentum is well-defined for this system - not always true for all operators]

→ Ok we can get p... and $T = \frac{p^2}{2M}$ right?

so how about:

$$\hat{T} = \frac{1}{2M} \hat{p}\hat{p} = \frac{-\hbar^2}{2M} \frac{\partial^2}{\partial x^2}$$

You can show this works, gives an eigenvalue for kinetic energy

$$T = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$$ ✓ works

⇒ same idea, for total energy we want to pull out ω $(E = \hbar\omega)$

so try: $\hat{E} = i\hbar \frac{\partial}{\partial t}$ → $E = \hbar\omega$ (check!)

⇒ Potential V is obviously totally general - and can be ugly! We will look at simple constant V terms, so $\hat{V} = V$, simple

- Now we are ready to sub in these operators into $T+V=E$ to get the..

Schrödinger equation:

$$-\frac{\hbar^2}{2M}\frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial \Psi(x,t)}{\partial t}$$

When V is time independent, we can factorise out the boring t dependence:

Time-Independent Schrödinger Eqn (TISE):

$$-\frac{\hbar^2}{2M}\frac{\partial^2 \Psi(x)}{\partial x^2} + V(x)\Psi(x) = -i\hbar\frac{\partial \Psi(x)}{\partial t}$$

or can rewrite as:

$$\underbrace{\left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + V(x)\right]}_{\text{'Hamiltonian'}}\Psi = E\,\Psi$$

$$\hat{H}\,\Psi = E\,\Psi$$

→ (Energy eigenvalue eqn)

We'll look at using this next week..

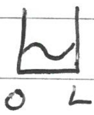
- 'Expectation Values' - like an 'average' of an observable

$\langle p_x \rangle$ tells me the number for p_x I get if I measure p_x many times and average the results

Sandwich the operator between ψ^*, ψ and integrate to find it:

> Example: operator for $\hat{x}$ just $= x$ so

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* x \psi \, dx$$

For our ∞ well friend 

...

$$\psi_1 = \sqrt{\frac{2}{L}} \sin kx \quad , \quad k = \frac{\pi}{L}$$

$$\Rightarrow \quad \langle x \rangle = \frac{2}{L} \int_0^L x \sin^2 \frac{\pi}{L} x \, dx$$

$$= \frac{2}{2L} \int_0^L x \left(1 - \cos \frac{2\pi}{L} x\right) dx$$

$$= \frac{1}{L} \left[\frac{x^2}{2}\right]_0^L - \frac{1}{L} \int_0^L x \cos \frac{2\pi}{L} x \, dx$$

For the $\int$ term, integrate by parts

as [an exercise!]

using $v = \frac{L}{2\pi} \sin \frac{2\pi}{L} x$, $u = x$

and show it $= 0$

$$\Rightarrow \langle x \rangle = \frac{1}{L} \left[\frac{x^2}{2} \right]_0^L$$

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

Which makes sense! We expect the particle, on average, to be in the middle.

- To conclude:
  - Operators pull out observables from the wavefn
  - Build operators for T, E, V and sub into $T + V = E$ to get Schrödinger Eqn
  - Expectation values from eg $\int \psi^* \hat{p} \psi \, dx$ for things without well-defined eigenvalues