Lecture 5 - Schrödinger eq

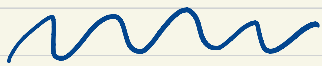
de' Broglie posits duality

particles

$F = ma$

waves

$$\frac{\partial \psi}{\partial t} = \frac{1}{v^2}\frac{\partial^2 \psi}{\partial x^2}$$



How to unify?

Dirac poses this problem to Schrödinger (1925) (Nobel prize, 1933)

Combined classical wave eq + cons of E + de Broglie to give the

single-particle, time-dependent wave eq

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right\}\Psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)$$

Steady-state, time-independent

Separate, $\Psi(\vec{r},t) = \psi(\vec{r})\,\phi(t)$, $\phi(t) = e^{iEt/\hbar}$

$$\Big\{ \underbrace{-\frac{\hbar^2}{2m_e}\nabla^2}_{KE} + \underbrace{V(\vec{r})}_{PE} \Big\} \psi(\vec{r}) = \underbrace{E}_{\text{total energy}}\psi(\vec{r})$$

"Hamiltonian"

Laplacian

Partial differential eq, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Let's disassemble, for e^- in H atom

$$V(\vec{r}) = -\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{|\vec{r}|}$$

$$\Big\{ \frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{|\vec{r}|} \Big\} \psi(\vec{r}) = E\psi(\vec{r})$$

Eigenvalue equation

Will have an infinite # of discrete sol'ns

$E_1 \quad \psi_1(\vec{r})$

$E_2 \quad \psi_2(\vec{r})$

$\cdots$

The E_i are the possible stable energy states of the e^- – the quantized states.

Schrödinger solved this and, voila, got E_i that agree exactly w/ Bohr.

The ψ_i turn out to be what you know as 1s, 2s, ...

These are de'Broglie's waves, but their meaning?

Max Born (1926) set out most widely accepted interpretation of ψ_i

- $\psi_i(\vec{r})$ is a probability amplitude, $\frac{1}{V^{1/2}}$
- $\psi_i^*(\vec{r}) \cdot \psi_i(\vec{r})$ is a probability density $(1/V)$
- $\int \psi_i^* \psi_i \, dr$ is a probability to find the particle of interest in the integration volume

Postulates of QM

John von Neumann, Mathematical Foundations of QM, 1932

(extensions to incorporate light, relativity, and gravity, have succeeded to various extents)

I. The physical state of a system is completely described by

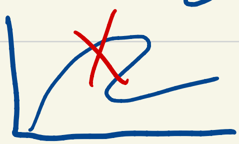
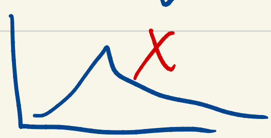
$\Psi(\vec{r}, t)$ - time dependent $\quad \psi(\vec{r})$ - time independent

ψ is in general complex, eg e^{ikx}

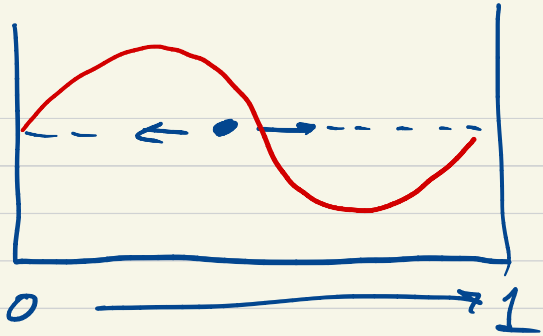
Will occassionally need complex conjugate $\quad \psi = e^{ikx} \quad \psi^* = e^{-ikx}$

ψ has to be "nice":

- single-valued
- continuous & twice-differentiable
- square-integrable


Example



$\psi(x) = \sin 2\pi x \qquad 0 < x < 1$

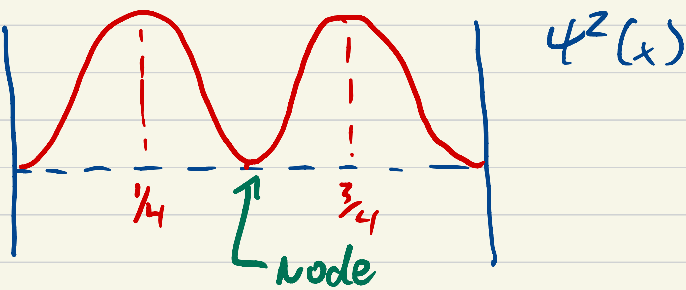
- acceptable? continuous ✓, differentiable ✓

$$\int_0^1 \psi^* \cdot \psi \, dx = \int_0^1 \sin^2 2\pi x \, dx = \frac{1}{2}$$

(Wolfram-Alpha)

square-integrable ✓

- most probable location?



- least probable? 0, 1/2, 1

- Probability to be $0 < x < 1/3$
Ie, to look & find particle in that range?

$P(x) = \psi^* \psi = \sin^2 2\pi x$

Normalize $P(x)$

$\int_0^1 P(x)\,dx = 1/2 \rightarrow \tilde{P}(x) = 2\sin^2 2\pi x$

Normalized ψ? $\sqrt{2}\sin 2\pi x$

$\tilde{\psi} = \psi/\sqrt{N} \quad N = \int \psi^* \psi\, dx$

$P(0 < x < \frac{1}{3}) = \int_0^{1/3} (\sqrt{2}\sin 2\pi x)^2\, dx$

$\approx 2/5$

II To every physical observable M there corresponds a QM operator $\hat{M}$. The only observable values of M are the eigenvalues of $\hat{M}$.

What's an "operator"? Something that operates on a function.

$f(x) = e^x$

$\hat{M}$	$\hat{M} f$	
$7\cdot$	$7e^x$	
$x\cdot$	xe^x	
d/dx	e^x	eigenftn!

If $\hat{M} f(x) = \text{constant}\, f(x)$

$f(x) \rightarrow$ eigenfunction   constant $\rightarrow$ eigenvalue

See Table of operators. Eg,

$\hat{x} = x\cdot \qquad \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \qquad \ldots$

QM operators are Hermitian

- eigenvalues are real numbers
- eigenfunctions are orthogonal

$$\hat{M}\phi_1 = m_1 \phi_2$$
$$\hat{M}\phi_2 = m_2 \phi_2$$
$$\vdots$$

m_i are real

ϕ_i are always normalizable

$$\int \phi_i^* \phi_i \, d\vec{r} = 1$$

and orthogonal

$$\int \phi_i^* \phi_j \, d\vec{r} = 0$$

More succinctly,

$$\int \phi_i^* \phi_j \, d\vec{r} = \langle \phi_i | \phi_j \rangle = \delta_{ij}$$

Example $\tilde{\psi}(x) = \sqrt{2}\sin 2\pi x$

- Is $\tilde{\psi}(x)$ an eigenfunction of the KE operator?

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 \longrightarrow -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \text{ in 1D}$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\tilde{\psi}(x) = \left(-\frac{\hbar^2}{2m_e}\right)\sqrt{2}\cdot(4\pi^2)(-\sin 2\pi x)$$

$$= \frac{4\pi^2\hbar^2}{2m}\cdot\sqrt{2}\sin 2\pi x$$

eigenfunction? YES

eigenvalue? $\frac{4\pi^2\hbar^2}{2m}$

- If we measured KE many times on identical particles, what would we get?

- Is $\tilde{\psi}(x)$ an eigenfunction of the position operator?

$$\hat{x}\cdot\tilde{\psi}(x) = x\cdot\tilde{\psi}(x)$$ NO!

So where is the particle? Can predict with some probability, as shown above.

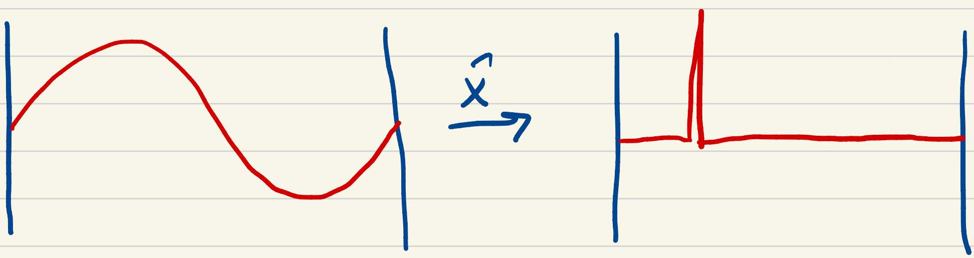
If we look, we will find it somewhere.

($\hat{x}\,\phi(x) = x_0\,\phi(x)$ $\quad x_0 \in \mathbb{R}$

$\phi(x) = \delta(x - x_0)$)

(Think of double slit expt)

But, when we look, its wavefunction will collapse to what we find!)



III If we measure $\hat{M}$ many times on identical systems in ψ, the <u>average result</u> will be the <u>expectation value</u> of $\hat{M}$.

$$\langle M \rangle = \int \psi^* (\hat{M}\psi)\, d\vec{r} = \langle \psi | \hat{M} | \psi \rangle$$

<u>Example</u> $\tilde{\psi}(x) = \sqrt{2} \sin 2\pi x$

$$\langle KE \rangle = \int_0^1 \tilde{\psi}(x) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) (\sqrt{2} \sin 2\pi x)\, dx$$

$$= \frac{4\pi^2\hbar^2}{2m} \cdot \cancelto{1}{\int_0^1 \tilde{\psi}(x)\, \psi(x)\, dx}$$

$$= \frac{4\pi^2\hbar^2}{2m}$$

$$\langle \tilde{\psi} | \hat{T} | \tilde{\psi} \rangle = \frac{4\pi^2\hbar^2}{2m} \cancelto{1}{\langle \tilde{\psi} | \tilde{\psi} \rangle} = \frac{4\pi^2\hbar^2}{2m}$$

expectation value of an eigenfunction is the eigenvalue position?

$$\langle x\rangle = \langle\tilde{\psi}|x|\tilde{\psi}\rangle = \int_0^1 x\cdot(2\sin^2\pi x)\,dx$$

$$= 1/2$$

momentum? $\hat{p} = -i\hbar\frac{d}{dx}$

$$\langle\tilde{\psi}|\hat{p}|\tilde{\psi}\rangle = ?$$

$$\hat{p}|\tilde{\psi}\rangle = -i\hbar\frac{d}{dx}\sqrt{2}\sin 2\pi x$$

$$= -i\hbar 2\pi\left(\sqrt{2}\cos 2\pi x\right)$$

$$\langle\tilde{\psi}|\hat{p}|\tilde{\psi}\rangle = -i\hbar 2\pi\int_0^1 \underbrace{2\sin 2\pi x\cos 2\pi x}_{\to 0}\,dx$$

$$= 0\ !!$$

Wait? How can the particle have KE but no momentum?

No momentum on average, but

$$|p| = \sqrt{2mKE} = 2\pi\hbar$$

Equally likely to be $\pm 2\pi\hbar$!!

Called a superposition state

Particle is equally likely to be going to the left and right.

Schrödinger's cat

entanglement

($\hat{p}$ eigenvectors are e^{ikx}, $\hbar k$

$$\tilde{\psi} = \frac{1}{\sqrt{2}}\left(e^{2\pi i \hbar x} + e^{-2\pi i \hbar x}\right)$$)

IV The time-invariant, constant E states of a system are sol'ns to the Schrödinger eq

$$\hat{H}\psi = E\psi \quad , \quad \hat{H} = \hat{T} + \hat{V}$$

V The uncertainty principle

Werner Heisenberg, 1927

"Impossible to specify simultaneously and to arbitrary precision both the position and momentum of a particle."

Later, generalized to all operators that do not commute

$$\hat{x}(\hat{p}\psi) \neq \hat{p}(\hat{x}\psi)$$

$$\Rightarrow \Delta p_x \cdot \Delta x \geq \hbar/2$$

Where $\Delta p_x = \left(\langle p^2 \rangle - \langle p \rangle^2\right)^{1/2}$

(In general, $\Delta A \Delta B \geq \frac{1}{2} \left| \langle [\hat{A}, \hat{B}] \rangle \right|$)

example

	car	electron
m	$1000\ kg$	$9\times10^{-31}\ kg$
v	$100\ km/hr$	$100\ km/hr$
p	$2.8\times10^{4}\ kg\ m/s$	$2.5\times10^{-29}\ kg\ m/s$

Suppose we want to know v to w/i 1 ppm

Δp	$2.8\times10^{-2}\ kg\ m/s$	$2.5\times10^{-35}\ kg\ m/s$
Δx	$1.9\times10^{-33}\ m$	$2.1\ m$
	unmeasurable	wow!!

As we squeeze a wavefunction, s.t. it becomes more like an eigenfunction of $\hat{p}$, so $\Delta p \to 0$, it spreads out so $\Delta x \to \infty$

Has important physical consequences, as we'll see!!