Schrodinger Equation

- The equation describing the evolution of $\Psi(x,t)$ is the Schrodinger equation

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

  - Given suitable initial conditions ($\Psi(x,0)$) Schrodinger's equation determines $\Psi(x,t)$ for all time

- This is analogous Newton's 2nd law

$$m\frac{d^2x}{dt^2}=-\frac{\partial V(x)}{\partial x}$$

  - Given suitable initial conditions (x(0), v(0)) Newton's 2nd law determines x(t) for all time

Schrodinger Equation

- We take Schrodinger's equation as one of the postulates of quantum mechanics
- Schrodinger himself just "figured it out"
- Thus there is no formal proof
  - We rely on comparison of its predictions with experiment to validate it
- But we'll briefly try to motivate it

Schrodinger Equation

- We'd like the quantum wave equation
  - To be consistent with de Broglie-Einstein relations
  - To be consistent with $E = T+V = p^2/2m+V$
  - To be linear in $\Psi(x,t)$
    - This means if Ψ_1 and Ψ_2 are solutions, then $c_1\Psi_1 + c_2\Psi_2$ is a solution
  - To have traveling wave solutions for a free particle (the case where $V(x,t)=0$)

Schrodinger Equation

- The first two assumptions can be combined into

$$E = \frac{p^2}{2m} + V$$

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + V$$

- The third assumption means that the wave equation can only contain terms like Ψ or its derivatives (no constants or higher order powers)

Schrodinger Equation

- Recall some of our solutions to the classical wave equation

$$\sin(kx-\omega t) \text{ or } e^{i(kx-\omega t)}$$

- Note that

$$\frac{\partial^2}{\partial x^2} \text{ gives a factor of } \mathrm{k}^2$$

$$\frac{\partial}{\partial t} \text{ gives a factor of } \omega$$

- Thus we might guess a wave equation that looks like

$$\alpha\frac{\partial\Psi}{\partial t}=\beta\frac{\partial^2\Psi}{\partial x^2}+V\Psi$$

Schrodinger Equation

- We could evaluate the constants α and β using the exponential free particle solution and find

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

- But we normally take Schrodinger’s equation as one of the postulates of quantum mechanics

Schrodinger Equation

- Does Ψ(x,t) = Asin(kx-ωt) satisfy the Schrodinger equation?
  - No

$$\frac{\partial \Psi}{\partial t} = -\omega A \cos(kx - \omega t)$$

$$\frac{\partial \Psi}{\partial x} = kA \cos(kx - \omega t)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -k^2 A^2 \cos(kx - \omega t)$$

$$-i\hbar\omega A \cos(kx - \omega t) = \left(\frac{\hbar^2 k^2}{2m} + V\right) A \sin(kx - \omega t)$$

  - And recall Asin(kx-ωt) was a solution to the classical wave equation

Schrodinger Equation

- Does Ψ(x,t) = Aexp{i(kx-ωt)} satisfy the Schrodinger equation?
  - Yes

$$\frac{\partial \Psi}{\partial t} = -i\omega A e^{i(kx-\omega t)}$$

$$\frac{\partial \Psi}{\partial x} = ikA e^{i(kx-\omega t)}$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -k^2 A e^{i(kx-\omega t)}$$

$$-i\hbar(i\omega) = \left(\frac{\hbar^2 k^2}{2m} + V\right)$$

$$E = \frac{p^2}{2m} + V$$

  - We'll see later if this solution can represent a physical state of the particle

Quantum Mechanics

- Postulate 1
  - Describes the system
  - The state of a physical system is defined by specifying the wave function $\psi(x,t)$

Wave Function

- Properties of $\Psi(x,t)$
  - $\Psi(x,t)$ must satisfy the Schrodinger equation
  - $\Psi(x,t)$ must be defined everywhere, finite, and single-valued
  - $\Psi(x,t)$, $d\Psi(x,t)/dx$ must be continuous (except when $V(x)$ is infinite)
  - $\Psi(x,t) \rightarrow 0$ as $x \rightarrow \pm\infty$ so that $\Psi(x,t)$ can be normalized
    - Or $\int dx|\Psi(x,t)|^2$ must be finite

Wave Function

- In quantum mechanics, we are working with the set of square integrable functions
- This set is called L^2 and has the structure of a Hilbert space
- If we further restrict the functions to be regular (defined everywhere, ...), the set is called F (a subspace of L^2) and it is a vector space
- Thus you can apply your knowledge of vector spaces to wave functions

Wave Function

- It is easy to see that if $\Psi(x,t)$ is a solution to the Schrodinger equation then $A\Psi(x,t)$ is also a solution

$$\int_{-\infty}^{\infty} dx P(x,t) = 1$$

$$\text{if } \int_{-\infty}^{\infty} dx \left|\Psi(x,t)\right|^2 = C, \text{ then } A^2 = \frac{1}{C}$$

- We can use A to normalize $\Psi(x,t)$ in cases where it isn't already
- This is always possible if $\Psi(x,t)$ is square integrable

$$\int_{-\infty}^{\infty} dx \left|\Psi(x,t)\right|^2 < \infty$$

Wave Function

- What is the normalization constant for $\Psi(x,t)=A\exp(-x^2/2a^2)$?

$$\int_{-\infty}^{\infty} dx \left|\Psi(x,t)\right|^2 = A^2 \int_{-\infty}^{\infty} dx e^{-\frac{x^2}{a^2}} = 1$$

$$A^2 a \sqrt{\pi} = 1$$

$$A = a^{-1/2} \pi^{-1/4}$$

Wave Function

- Will the wave function normalization change with time?

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}$$

$$-i\hbar\frac{\partial\Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2} \text{ (take the complex conjugate)}$$

now $P(x,t) = \Psi^*\Psi$ so

$$\frac{\partial P}{\partial t} = \frac{\partial\Psi^*}{\partial t}\Psi + \Psi^*\frac{\partial\Psi}{\partial t}$$

then

$$\frac{\partial P}{\partial t} = \frac{1}{i\hbar}\left(\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2}\Psi - \frac{\hbar^2}{2m}\Psi^*\frac{\partial^2\Psi}{\partial x^2}\right)$$

Wave Function

- Continuing on

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{\hbar}{2im}\left(\Psi^*\frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi\right)\right]$$

we define the probability current $j(x,t)$ as

$$j(x,t) = \left[\frac{\hbar}{2im}\left(\Psi^*\frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi\right)\right]$$

we define the probability density $P(x,t) = \Psi^*\Psi$

Thus we are led to the continuity equation

$$\frac{\partial}{\partial t}P(x,t) + \frac{\partial}{\partial x}j(x,t) = 0$$

Wave Function

- To answer the question note

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty} dx P(x,t) = -\int_{-\infty}^{\infty} dx \frac{\partial}{\partial x} j(x,t) = 0$$

since for square integrable functions

$j(x,t) \to 0$ as $x \to \pm\infty$

- This means if Ψ(x,t) is normalized at t=0, it stays normalized for all future times (even though the wave function is evolving through Schrodinger's equation)

Quantum Mechanics

- Postulate 2
  - Describes physical quantities
  - Every measurable physical quantity O is described by an operator O-hat that acts on the wave function ψ

Operators

- Some examples of operators are

energy E	$i\hbar\frac{\partial}{\partial t}$
momentum p	$-i\hbar\frac{\partial}{\partial x}$
position x	x
parity P	$P\Psi(x) = \Psi(-x)$

- And remember, each physical observable is described by some operator

Operators

- Momentum operator

$$\text{let } \Psi = e^{i(kx\text{-}\omega x)}$$

$$\frac{\partial \Psi}{\partial x} = \frac{\partial}{\partial x}\left(e^{i(kx\text{-}\omega x)}\right) = ike^{i(kx\text{-}\omega x)} = ik\Psi = i\frac{p}{\hbar}\Psi$$

$$p\Psi = -i\hbar\frac{\partial \Psi}{\partial x}$$

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}$$

Operators

- Energy operator

$$\text{let } \Psi = e^{i(kx\text{-}\omega x)}$$

$$\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial t}\left(e^{i(kx\text{-}\omega x)}\right) = -i\omega e^{i(kx\text{-}\omega x)} = -i\omega\Psi = -i\frac{E}{\hbar}\Psi$$

$$E\Psi = i\hbar\frac{\partial \Psi}{\partial t}$$

$$\hat{E} = i\hbar\frac{\partial}{\partial t}$$

Operators

- An easy way to remember the Schrodinger equation is

$$E = T + V$$

$$E = \frac{p^2}{2m} + V$$

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

- The Hamiltonian operator is

$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}$$

Operators

- Most of the operators we will study are linear

$$\text{If } \Psi \in F, \text{then } \Psi' = \hat{\mathrm{O}}\Psi \in F$$

$$\text{and } \hat{\mathrm{O}}(\mathrm{c}_1\Psi_1 + c_2\Psi_2) = \mathrm{c}_1\hat{\mathrm{O}}\Psi_1 + \mathrm{c}_2\hat{\mathrm{O}}\Psi_2$$

- The product of two linear operators is defined to be

$$\hat{A}\hat{B}\Psi = \hat{A}\left(\hat{B}\Psi\right)$$

- In general

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

$$\left[\hat{A},\hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$$

$\left[\hat{A},\hat{B}\right]$ is called the commutator of $\hat{A}$ and $\hat{B}$

Quantum Mechanics

- Postulate 3
  - Describes measurement
  - The only possible result of a measurement of a physical quantity O is one of the eigenvalues of the corresponding operator O-hat

Measurement

- The eigenvalue equation looks like

$$\hat{O}u_n = o_n u_n$$

o_n are the eigenvalues

u_n are the eigenvectors

u_n are wave functions like Ψ

- A Hermitian operator is defined by the property

$$\int dx \Psi^* \hat{O} \Psi = \int dx \left(\hat{O}\Psi\right)^* \Psi$$

Measurement

- Two properties of Hermitian operators are
  - Eigenvalues of Hermitian operators are real
    - This is good since the eigenvalues correspond to the result of a physical measurement!
  - Eigenvectors of Hermitian operators corresponding to different eigenvalues are orthogonal

Measurement

- Proof that eigenvalues are real

$$\text{let } \hat{A}u_a = au_a$$

$$\int u_a^* A u_a dx = \int \left(Au_a\right)^* u_a dx$$

$$a\int u_a^* u_a dx = a^* \int u_a^* u_a dx$$

$$a = a^*$$

Measurement

- Proof that eigenvectors are orthogonal

$$\text{let } \hat{A}u_a = au_a \text{ and } \hat{A}u_b = bu_b, a \neq b$$

$$\int u_a^* A u_b dx = \int \left(Au_a\right)^* u_b dx$$

$$b\int u_a^* u_b dx = a^* \int u_a^* u_b dx$$

$$\left(b-a\right)\int u_a^* u_b dx = 0$$

$$\int u_a^* u_b dx = 0$$

- $\int u_a^* u_b dx$ is called the scalar or inner product
- $\int u_a^* u_b dx = 0$ is the orthogonality condition

Expectation Values

- Recall from probability the definition of mean

$$\langle x \rangle = \int_{-\infty}^{\infty} dx\, x P(x)$$

- In quantum mechanics we define

$$\langle x \rangle = \int_{-\infty}^{\infty} dx\, x \left| \Psi(x,t) \right|^2$$

- More generally we define the expectation value

$$\langle \hat{O} \rangle = \int_{-\infty}^{\infty} dx \Psi^* \hat{O} \Psi$$

Expectation Values

- The expectation value tells you the average value of the observable that has been measured

Expectation Values

Consider

$$\hat{O}u_n = o_n u_n$$

Then

$$\left\langle \hat{O} \right\rangle = \int dx\, u_n^* \hat{O} u_n = o_n \int dx\, u_n^* u_n = o_n$$

Moreover let

$$\hat{O}u_a = a u_a$$

$$\hat{O}u_b = b u_b$$

Then if $\Psi = c_a u_a + c_b u_b$

$$\left\langle \hat{O} \right\rangle = a\left|c_a\right|^2 + b\left|c_b\right|^2$$