Quantum Mechanics

Postulate 4

- Describes expansion
- In the eigenvalue equation $\hat{O}u_i = o_i u_i$ the eigenfunctions $\{u_i\}$ constitute a complete, orthonormal set

$$\int_{-\infty}^{\infty} dx\, u_i^*(x) u_j(x) = \delta_{ij} \text{ is called the orthonormality relation}$$

- The set of eigenfunctions $\{u_i\}$ form a basis: any wave function Ψ can be expanded as a coherent superposition of the complete set

$$\text{For any } \Psi(x) \in F, \text{ it can be written as}$$

$$\Psi(x) = \sum_i c_i u_i(x)$$

Expansion

- Thus you can write any wave function in terms of wave functions you already know. The coefficients can be evaluated as

$$\int_{-\infty}^{\infty} dx\, u_j^* \Psi = \int_{-\infty}^{\infty} dx\, u_j^* \sum_i c_i u_i$$

$$= \sum_i c_i \int_{-\infty}^{\infty} dx\, u_j^* u_i$$

$$= \sum_i c_i \delta_{ji}$$

$$= c_j$$

Expansion

- The expectation value can be written using the $\{u_i\}$ basis

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

$$= \int_{-\infty}^{\infty} dx \sum_i c_i^* u_i^* \hat{O} \sum_j c_j u_j$$

$$= \sum_i \sum_j c_i^* c_j \int_{-\infty}^{\infty} dx\, u_i^* o_j u_j$$

$$= \sum_j |c_j|^2 o_j$$

- Thus the probability of observing o_j when O is measured is $|c_j|^2$

Quantum Mechanics

- Postulate 5
  - Describes reduction
  - After a given measurement of an observable O that yields the value o_i, the system is left in the eigenstate u_i corresponding to that eigenvalue
  - This is called the collapse of the wavefunction

Reduction

- Before measurement of a particular observable of a quantum state represented by the wave function Ψ, many possibilities exist for the outcome of the measurement
- The wave function before measurement represents a coherent superposition of the eigenfunctions of the observable
  - $\Psi = (u_{\text{cat dead}} + u_{\text{cat alive}})$

Reduction

- The wave function immediately after the measurement of O is u_i if o_i is observed
  - $|c_j|^2 = \delta_{ij}$
- Another measurement of O will yield o_i since the wave function is now o_i, not Ψ
  - If you look at the cat again it's still dead (or alive)

Quantum Mechanics

Postulate 6

- Describes time evolution
- Between measurements, the time evolution of the wave function is governed by the Schrodinger equation

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

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$

$\hat{H}$ is the Hamiltonian operator $\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2m} + \hat{V}$

Time Independent Schrodinger Equation

- How do we solve Schrodinger's equation?
  - In many cases, V(x,t) = V(x) only
  - Apply the method of separation of variables

$$\Psi(x,t) = \psi(x) f(t)$$

$$\text{then } \frac{\partial \Psi}{\partial t} = \psi \frac{df}{dt} \text{ and } \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2 \psi}{dx^2} f$$

and Schrodinger's equation now reads

$$i\hbar \psi \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} f + V \psi f$$

$$i\hbar \frac{1}{f} \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2 \psi}{dx^2} + V$$

Time Independent Schrodinger Equation

- The last equation shows that both sides must equal a constant (since one is a function of t only and the other a function of x only)

$$\text{(left)}\; i\hbar \frac{1}{f}\frac{df}{dt} = E$$

$$\text{or} \qquad \frac{df}{dt} = -\frac{iE}{\hbar} f$$

$$\text{(right)} -\frac{\hbar^2}{2\text{m}}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

- Thus we've turned one PDE into two ODE's using separation of variables

Time Independent Schrodinger Equation

- Time dependent piece

$$\frac{df}{dt} = -\frac{iE}{\hbar} f$$

$$\text{has solution } f = Ce^{-\frac{iEt}{\hbar}} = Ce^{-i\omega t}$$

$$\text{We can absorb } C \text{ into the } \psi \text{ so}$$

$$f(t) = e^{-\frac{iEt}{\hbar}}$$

- Note the $e^{-i\omega t}$ has the same time dependence as the free particle solution
  - Thus we see $E = \hbar\omega$

Time Independent Schrodinger Equation

- Time independent piece

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

- Comment 1
  - Recall our definition Hamiltonian operator H

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

Then we have

$$\hat{H}\psi=E\psi$$

Time Independent Schrodinger Equation

➢Comment 2

$\hat{H}\psi = E\psi$ is an eigenvalue equation

E are the eigenvalues

ψ are the eigenvectors

- The allowed (quantized) energies are the eigenvalues of the Hamiltonian operator H
- In quantum mechanics, there exist well-determined energy states

Time Independent Schrodinger Equation

Comment 3

- Wave functions that are products of the separable solutions form stationary states

Always remember the full wave function is

$$\Psi(x,t)=\psi(x)e^{-\frac{iEt}{\hbar}}$$

Note the probability density

$$|\Psi(x,t)|^2=\Psi^*\Psi=\psi^* e^{+\frac{iEt}{\hbar}}\psi e^{-\frac{iEt}{\hbar}}=|\psi(x)|^2$$

- The probability density is time independent
- All the expectation values are time independent
- Nothing ever changes in a stationary state

Time Independent Schrodinger Equation

- Comment 4

$$\langle H \rangle = \int_{-\infty}^{\infty} dx\, \psi^* \hat{H} \psi = E \int_{-\infty}^{\infty} dx\, \psi^* \psi = E$$

$$\text{Also } \hat{H}^2 \psi = \hat{H}\left(\hat{H} \psi\right) = \hat{H} E \psi = E \hat{H} \psi = E^2$$

$$\text{Then } \left\langle H^2 \right\rangle = \int_{-\infty}^{\infty} dx\, \psi^* \hat{H}^2 \psi = E^2 \int_{-\infty}^{\infty} dx\, \psi^* \psi = E^2$$

$$\text{So } \sigma_{\mathrm{H}}^2 = \left\langle H^2 \right\rangle - \left\langle H \right\rangle^2 = 0$$

- In stationary states, every measurement of the total energy is a well-defined energy E

Time Independent Schrodinger Equation

➢ Comment 5

- A general solution to the time dependent Schrodinger equation is

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}$$

Free Particle

- Free particle means V=0 everywhere
- You'd think that this would be the easiest problem to solve

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

$$\frac{d^2\psi}{dx^2} = -k^2\psi \text{ where } k = \frac{\sqrt{2mE}}{\hbar}$$

General solution can be written as

$$\psi = Ae^{ikx} + Be^{-ikx}$$

While this wave function is a solution it is not normalizable

Free Particle

- Let's look at the momentum eigenvalue equation

$$\hat{p}u_p(x) = -i\hbar\frac{\partial u_p(x)}{\partial x} = pu_p(x)$$

There is no constraint on p so the eigenvalues are continuous

The solution is $u_p(x) = Ce^{ipx/\hbar} = Ce^{ikx}$

We expect these eigenfunctions to satisfy the orthonormality condition

$$\int_{-\infty}^{\infty} dx\, u_{p'}^*(x)u_p(x) = |C|^2\int_{-\infty}^{\infty} dx e^{i(p-p')x/\hbar}$$

$$= |C|^2 2\pi\hbar\,\delta(p-p')$$

letting $C = \frac{1}{\sqrt{2\pi\hbar}}$

$$\int_{-\infty}^{\infty} dx\, u_{p'}^*(x)u_p(x) = \delta(p-p')$$

Properties of the δ Function

$$\delta(x) = \{0 \text{ for } x \neq 0, \infty \text{ for x} = 0\}$$

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

$$\int_{-\infty}^{\infty} dx f(x) \delta(x-a) = f(a)$$

$$\delta(x - x_0) = \int_{-\infty}^{\infty} dk e^{ik(x-x_0)}$$

Free Particle

- This is the orthonormality condition for continuous eigenfunctions

$$\int_{-\infty}^{\infty} dx\, u_i^*(x) u_j(x) = \delta_{ij} \quad \text{(discrete)}$$

$$\int_{-\infty}^{\infty} dx\, u_{p'}^*(x) u_p(x) = \delta(p - p') \quad \text{(continuous)}$$

Free Particle

- Back to our e^{ikx} normalization dilemma
  - Solution 1 - Confine the particle in a very large box
    - We'll work this problem next time

Free Particle

- Back to our e^{ikx} normalization dilemma
  - Solution 2 – Use wave packets

    Since the $u_p(x)$ form a complete set

    $$\psi(x) = \int_{-\infty}^{\infty} dp\, a(p) \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$$

  - Look familiar? Remember

    $$\Psi(x,0) = \int_{-\infty}^{\infty} dk A(k) e^{ikx}$$

    then $A(k)$ is the Fourier transform of $\Psi(x,0)$

    $$A(k) = \int dx \Psi(x,0) e^{-ikx}$$

  - Thus by using a sufficiently peaked momentum distribution, we can make space distribution so broad so as to be essentially constant