Wave function, Operators
and
Schrödinger Wave Equation

Wave function

A microscopic particle is described by a **wave function** (ψ) which contains all the information about the physical properties of the particle.

In one dimension $\Psi(x,t)$

The probability of finding the particle between *x* and *x+dx* at time t is given by

$$\left|\Psi(x,t)\right|^2 dx$$

Normalization: The probability of finding the particle somewhere should be **one**. This in one-dimension would mean the following.

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

Operator:

An operator $(\hat{O})$ is one that turns functions into functions. Example: The derivative operator $O = \dfrac{d}{dx}$

$$\hat{O}f(x) = \frac{d}{dx}f(x) \qquad if\ \ f(x) = \sin kx \qquad \hat{O}f(x) = k\cos kx$$

In quantum physics we come across several operators.

For every physical quantity there is an operator.

Consider an operators $\hat{A}$ such that

$\hat{A}\Psi(x,t) = \alpha\Psi(x,t)$ *where α is called the eigenvalue.*

Ψ(x,t) is called eigenfunction belonging to the eigenvalue α.

In Quantum Physics, eigenvalues are related to Observables

Examples (common life)

$$\hat{A} = \frac{d}{dx} \qquad f(x) = e^{\alpha x} \qquad \hat{A}f(x) = \alpha e^{\alpha x} = \alpha f(x)$$

$$\hat{A} = \frac{d^2}{dx^2} \qquad f(x) = \sin bx + \cos bx \qquad \hat{A}f(x) = -b^2 f(x)$$

$$\hat{A} = x\frac{d}{dx} \qquad f(x) = ax^n \qquad \hat{A}f(x) = nf(x)$$

Commuting and Non-commuting Operators

Consider two operators A and B, and perform the operation

$$A\{B\,f(x)\} - B\{A\,f(x)\} = (AB - BA)\,f(x)$$

Notation: $[A, B] = AB - BA$ ***is called commutator***

Two operators A and B are said to be **commuting** if

$[A, B] = 0$ ***Order in which the operators operate is not important***

Two operators A and B are said to be **non commuting** if

$[A, B] \neq 0$ ***Order in which the operators operate is important***

Observables belonging to commuting operators can be measured simultaneously with unlimited precision. Observables of Non commuting operators follow Heisenberg uncertainty relation!

Expectation value:

It is the average value of an operator (O) that one would get after a very large number of measurements are made on identical systems.

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

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

How to obtain equation that governs the evolution of wave function?

Particle $$\overline{F} = m\frac{d^2\overline{r}}{dt^2}$$

Wave $$\frac{\partial^2 E}{\partial x^2} = \frac{1}{c^2}\frac{\partial E}{\partial t}$$

What about Ψ

de Broglie wave

$$\Psi(x,t) = Ae^{i(kx-\omega t)}$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p_x}{h} = \frac{p_x}{\hbar}$$

$$\omega = \frac{E}{\hbar}$$

$$\frac{\partial \Psi(x,t)}{\partial t} = -i\omega Ae^{i(kx-\omega t)} = -i\omega\Psi(x,t) = -\frac{iE}{\hbar}\Psi(x,t)$$

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = E\Psi(x,t)$$

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

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

on $\Psi(x,t)$ gives energy *E*

de Broglie wave

$$\Psi(x,t) = Ae^{i(kx-\omega t)}$$

$$\frac{\partial \Psi}{\partial x} = ikAe^{i(kx-\omega t)} = ik\Psi \quad = \frac{ip_x}{\hbar}\Psi$$

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

Momentum operator: $\hat{p}_x = -i\hbar\dfrac{\partial}{\partial x}$

Operation of $\hat{p}_x = -i\hbar\dfrac{\partial}{\partial x}$ **on** $\Psi(x,t)$ **gives momentum** p_x

Kinetic energy operator

Consider a nonrelativistic particle

$$K = KE = \frac{p_x^2}{2m} \qquad \hat{p}_x = -i\hbar\frac{\partial}{\partial x}$$

$$\hat{K} = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

Kinetic energy operator $= \dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$

Operation of $\hat{K} = \dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$ **on** $\Psi(x,t)$ **gives kinetic energy**

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

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\left(-i\hbar \frac{\partial}{\partial x}\right)\Psi(x,t)dx = -i\hbar \int_{-\infty}^{\infty} \Psi^*(x,t)\frac{\partial}{\partial x}\Psi(x,t)dx$$

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

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\left(i\hbar \frac{\partial}{\partial t}\right)\Psi(x,t)dx = i\hbar \int_{-\infty}^{\infty} \Psi^*(x,t)\frac{\partial}{\partial t}\Psi(x,t)dx$$

Kinetic energy operator $\hat{K} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

$$\langle K \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\Psi(x,t)dx = \frac{-\hbar^2}{2m}\int_{-\infty}^{\infty} \Psi^*(x,t)\frac{\partial^2}{\partial x^2}\Psi(x,t)dx$$

Energy operator $\hat{E} = i\hbar \frac{\partial}{\partial t}$ ***Momentum operator*** $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

Consider the following operation:

$$(xp_x - p_x x)\psi(x,t)$$

$$= x\left(-i\hbar \frac{\partial \psi(x,t)}{\partial x}\right) - \left(-i\hbar \frac{\partial}{\partial x}\right) x\psi(x,t)$$

$$= -i\hbar x \frac{\partial \psi(x,t)}{\partial x} + i\hbar \psi(x,t) + i\hbar x \frac{\partial \psi(x,t)}{\partial x} = i\hbar \psi(x,t)$$

$$Therefore,\ (xp_x - p_x x)\psi(x,t) = i\hbar \psi(x,t)$$

$$\therefore \quad xp_x - p_x x = i\hbar \quad \Rightarrow \quad [x, p_x] = i\hbar$$

Position and momentum operators do not commute!

Commutation relation between $\hat{K}$ and $\hat{p}$

$$\hat{K} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \qquad \hat{p}_x = -i\hbar\frac{\partial}{\partial x}$$

$$[\hat{K}, \hat{p}] = \hat{K}\hat{p} - \hat{p}\hat{K}$$

$$(\hat{K}\hat{p} - \hat{p}\hat{K})\psi(x,t)$$

$$= \left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\left(-i\hbar\frac{\partial}{\partial x}\psi(x,t)\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)\left(\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2}\right)$$

$$= \left(\frac{i\hbar^3}{2m}\frac{\partial^3}{\partial x^3} - \frac{i\hbar^3}{2m}\frac{\partial^3}{\partial x^3}\right)\psi(x,t) = 0(\psi(x,t))$$

$$\therefore [\hat{K}, \hat{p}] = \hat{K}\hat{p} - \hat{p}\hat{K} = 0$$

Kinetic energy operator and momentum operator commute

Constructing Schrodinger Wave Equation

(for a nonrelativistic particle in 1-d)

Kinetic energy operator $\hat{K} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

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

Energy = E = KE + PE

Writing in operator form $\hat{E}\Psi(x,t) = E\Psi(x,t)$

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

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

Schrodinger Equation

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

Time dependent Schrodinger Equation

Let the wave function be separable, $\Psi(x,t)=\psi(x)\phi(t)$

Introducing this for into the Time Dependent Schrodinger Equation

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

Divide both sides by $\Psi(x,t)=\psi(x)\phi(t)$

$$\frac{i\hbar\left(\partial\phi(t)/\partial t\right)}{\phi(t)}=\frac{-(\hbar^2/2m)(\partial^2\psi/\partial x^2)+V(x)\psi(x)}{\psi(x)}$$

$$\frac{i\hbar\left(\partial\phi(t)/\partial t\right)}{\phi(t)} = \frac{-(\hbar^2/2m)(\partial^2\psi/\partial x^2)+V(x)\psi(x)}{\psi(x)}$$

Left side is a function of *t* while right side is a function of *x*

$$\frac{i\hbar\left(\partial\phi/\partial t\right)}{\phi(t)} = \frac{-(\hbar^2/2m)(\partial^2\psi/\partial^2 x)+V(x)\psi(x)}{\psi(x)} = C$$

C is a constant!

$$\frac{i\hbar\left(\partial\phi(t)/\partial t\right)}{\phi(t)} = C \quad \Rightarrow \quad i\hbar\frac{\partial\phi}{\partial t} = C\phi$$

But, $i\hbar\dfrac{\partial}{\partial t} = \hat{E}$ is Energy operator $\Rightarrow$ $C = E$

$$\frac{i\hbar\left(\partial\phi/\partial t\right)}{\phi(t)} = \frac{-(\hbar^2/2m)(\partial^2\psi/\partial x^2) + V(x)\psi(x)}{\psi(x)} = E$$

$$i\hbar\frac{\partial\phi(t)}{\partial t} = E\phi(t)$$

$$\phi(t) = e^{-iEt/\hbar} = e^{-i\omega t}$$

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

$\psi(x)$ ***is to be determined from***

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x)$$

Time independent Schrodinger Equation

Separability of wave function $\Psi(x,t) = \psi(x)\phi(t)$

It permits us to solve time independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x) = E\psi(x)$$

and get $\psi(x)$ and the energy eigen values (E) of a given problem. These are related to the 'stationary' states.

Normalization

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

$$\left|\Psi(x,t)\right|^2 = \left|\psi(x)\right|^2$$

Hamiltonian (H)

Time independent Schrodinger Equation

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\psi(x)=E\psi(x)$$

$$H=KE+PE=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)$$

$$H\psi(x)=E\psi(x)$$

E is an eigenvalue and ψ is an eignfunction.

Energy can also be found from the expectation value of H

$$\langle E\rangle=\int_{-\infty}^{\infty}\psi^*(x)H\psi(x)dx=\int_{-\infty}^{\infty}\psi^*(x)\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\psi(x)dx$$

Time independent Schrodinger Equation

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\psi(x)=E\psi(x)$$

$\psi(x)$ must be everywhere finite, single-valued, and continuous.

$\psi(x)$ must be “smooth” that is, the slope of the wave $d\psi/dx$ also must be continuous wherever $V(x)$ has a finite value.

Solution is subject to the ‘boundary’ conditions of a given problem.

Generalization to 3-d

$$H=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(x,y,z)\ =-\frac{\hbar^2}{2m}\nabla^2+V(x,y,z)$$

$$i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t}=H\Psi(x,y,z,t)$$

$$=-\frac{\hbar^2}{2m}\nabla^2\Psi(x,y,x,t)+V(x,y,z)\Psi(x,y,z,t)$$

After separation of variables $\Psi(x,y,z,t)=\psi(x,y,z)\phi(t)$

$$\phi(t)=e^{-iEt/\hbar}$$

$$H\psi(x,y,z)=E\psi(x,y,z)$$