Operators

We wrote the Schrödinger's equation

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi = E\Psi$$

or $$\hat{H}\Psi = E\Psi \quad \text{---} (1)$$

where $\hat{H}$ is the Hamiltonian operator.

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

What is an operator?

Operator is a mathematical expression that carries the information of one or successive operation.

Examples: '$\frac{d}{dx}$' is an operator

If we have a function, $f(x) = e^{-\alpha x}$, on which the operator operates, then we obtain the following,

$$\underbrace{\frac{d}{dx}}_{\text{Operator}}\Big(\underbrace{e^{-\alpha x}}_{\text{function}}\Big) = -\alpha \underbrace{e^{-\alpha x}}_{\text{New/the same function.}}$$

or $$\frac{d}{dx} f(x) = -\alpha f(x)$$

Does it look like $\hat{H}\Psi = E\Psi$?

Collect a few more examples of operators.

In quantum mechanics, we often denote an operator by putting a hat or cap on the operator. ~~such~~ For example we write $\hat{A}$. (A hat).

Notice in equation (1), the Hamiltonian Operator $\hat{H}$ operates on the wave function and provides the system's total energy and the function back.

Eigenvalue equations

In an equation, if an operator operates on a function and produces the same function then the function on which the operator operated is called the 'eigenfunction' and the equation is called eigenvalue equation.

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

$\hat{A}$ = operator

$f(x) = e^{\alpha x}$ eigenfunction of operator $\frac{d}{dx}$

α = eigenvalue.

The Schrödinger's equation is an eigenvalue equation.

(Operator)(Eigenfunction) = (Eigenvalue)(Eigenfunction)

The construction of operators

An Operators actually carries the ~~observa~~ information of an operator leading to an observable.

What is the operator for location along the x-axis?

It is $\hat{x} = x \times$,

Similarly for momentum operator it is

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

The Hamiltonian operator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x)$$

or, $$\hat{H} = \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)\left(-i\hbar\frac{d}{dx}\right)$$

or, $$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}(x)$$

For a potential of form $V(x) = \frac{1}{2}kx^2$

$\hat{V}(x) = \frac{1}{2}kx^2 \times$

Calculate $\langle x\rangle$, $\langle p\rangle$, $\langle T\rangle$ etc.

Commutator

Two operators $\hat{A}$ and $\hat{B}$ are said to commute if

$$\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x)$$ for an arbitrary operand.

The commutator of these two operators can now be written as,

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

If $\hat{A}\hat{B} = \hat{B}\hat{A}$, then $[\hat{A}, \hat{B}] = 0$, and we say $\hat{A}$ and $\hat{B}$ commute. If $\hat{A}\hat{B} \neq \hat{B}\hat{A}$, then they do not commute.

⇒ In quantum mechanics, the operators are usually linear having the following properties

$$\hat{A}[f(x) + g(x)] = \hat{A}f(x) + \hat{A}g(x) \quad \text{— (1)}$$

$$\hat{A}[cf(x)] = c\hat{A}f(x) \quad \text{— (2)}$$

Where $f(x)$ and $g(x)$ are arbitrary functions.

What is the physical significance of commutators?

If two operators do not commute, the eigenfunctions of one of the operators cannot be eigenfunctions of the other operator. In that case, we can only have a precise value of one of the operator's corresponding observable; the other property can be estimated as an average property.

Let's take the case of $[\hat{x}, \hat{p}_x] = i\hbar$

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

If we have an arbitrary function $\psi(x)$, on which $\hat{p}_x$ operates

$$-i\hbar \frac{d}{dx}\psi = \hbar k \psi \quad \text{— (1)}$$

The solution for eq^n (1) is $\psi = A\exp(-ikx)$

What can we say about the particle's position? Well, the particle can be anywhere on the x-axis; the position cannot be defined precisely.

Application of Schrödinger's equation

1. $$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V\right]\psi = E\psi$$

Where the Hamiltonian operator is

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{\text{Kinetic energy}} + \underbrace{V}_{\text{Potential Energy}}$$

Now, we will study a few systems by varying the 'V'.

1. Particle in a box

Infinite square well

$$V(x) = 0 \quad 0 \le x \le L$$
$$= \infty \quad \text{otherwise}$$

A particle of mass m is confined inside a 1-D box of length L. This particle is free to move inside the box ($V=0$) but is restricted on two ends ($x=0$) and ($x=L$) by infinite ($V\to\infty$) walls.

The Schrödinger's equation for this system can be written as

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+0\right]\psi = E\psi$$

or $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \quad \text{—(1)}$$

or $$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi$$

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

—(2)

The general solution to this equation is

$$\psi(x) = A \sin kx + B \cos kx \quad \text{—③}$$

Where A and B are arbitrary constants. that we'll evaluate soon.

Now let's check the boundary conditions $x=0$ and $x=L$ at which $\psi(x)=0$

For $x=0$ $\quad \psi(0) = A\sin(0) + B\cos(0)$

or $B = 0$

Hence, from eqn ③, we can write,

$$\psi(x) = A \sin kx \quad \text{—④}$$

Now, $x=L$ makes $\psi(L) = A \sin kL = 0$ as well.

or $\sin kL = 0$ | $A=0$ would make $\psi(x)=0$

or $kL = 0, \pm\pi, \pm 2\pi \ldots$

or $kL = n\pi$ where $n = 1, 2, 3 \ldots$

or $k = \frac{n\pi}{L}$ with $n = 1, 2, 3 \ldots$

Putting the value of k in eqn ④, we get

$$\psi(x) = A \sin \frac{n\pi x}{L} \quad \text{—⑤}$$

Now, we need to evaluate 'A'.

From the normalization condition,

$$\int_0^L |A|^2 \sin^2(kx)\, dx = 1$$

or $|A|^2 \frac{L}{2} = 1$

or $A = \sqrt{\frac{2}{L}}$

Finally the solutions of $\psi(x)$ are

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}}$$

We know $k = \frac{\sqrt{2mE}}{\hbar}$

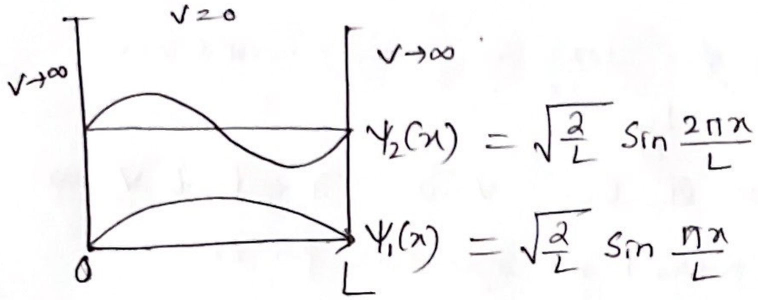
or $\frac{n\pi}{L} = \frac{\sqrt{2mE}}{\hbar}$

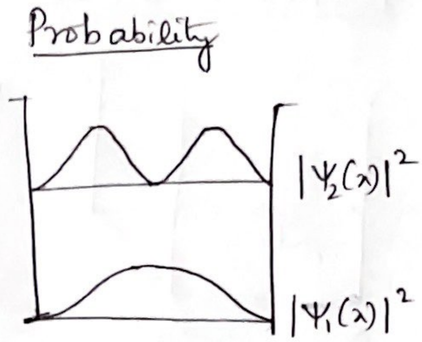
or $E = \frac{n^2 \hbar^2 \pi^2}{2mL^2}$

or $E = \frac{n^2\hbar^2\pi^2}{2mL^2}$

or $\boxed{E = \frac{n^2 h^2}{8mL^2}}$ $\quad \left(\hbar = \frac{h}{2\pi}\right)$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$





The time-independent Schrödinger's equation provided an infinite set of solutions $\psi_n(x)$ where $n = 1, 2, 3 \cdots$ where $\psi_1(x)$ is the ground state, the others having energies increase proportional to n^2 are called the excited states. These wavefunctions $\psi_n(x)$ have some interesting and important properties,

1. They are alternatively <u>even</u> and <u>odd</u> with respect to each other.

2. The ground state $\psi_1(x)$ has no node, but as we go up, the successive states have nodes $(n-1)$. For example $\psi_2(x)$ has node 1, $\psi_3(x)$ has two nodes etc.

3. These wavefunctions are mutually <u>orthogonal</u>, meaning

$$\int \psi_m^*(x)\, \psi_n(x)\, dx = 0 \quad (m \neq n)$$

or $$\delta_{mn} = 0$$

Homework

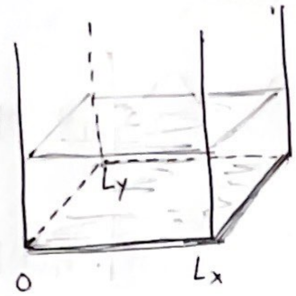
$$\int \psi_1(x)\psi_2(x)\, dx = 0$$

where δ_{mn} is called Kronecker delta

$$\delta_{mn} = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases}$$

If two wave functions satisfy the above conditions, we say that they are orthonormal.

⇒ Particle in 2-D box



Box lengths along the X- and Y- axes are L_x and L_y

Inside the box, $V=0$, and outside $V=\infty$

The Schrödinger equation for the particle inside the box is given by

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\Psi = E\Psi \quad -(1)$$

Eq (1) is a second-order partial differential equation.

Separation of variables

$$\Psi(x,y) = \psi(x)\,\psi(y)$$

Now, $\dfrac{\partial^2\Psi(x,y)}{\partial x^2} = \psi(y)\dfrac{d^2\psi(x)}{dx^2}$; $\dfrac{\partial^2\Psi(x,y)}{\partial y^2} = \psi(x)\dfrac{\partial^2\psi(y)}{\partial y^2}$

Putting these in eqn (1) we get

$$-\frac{\hbar^2}{2m}\left[\psi(y)\frac{\partial^2\psi(x)}{\partial x^2}+\psi(x)\frac{\partial^2\psi(y)}{\partial y^2}\right] = E\,\psi(x)\psi(y) \quad -(2)$$

Dividing eqn (2) by $\psi(x)\psi(y)$,

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} - \frac{\hbar^2}{2m}\frac{1}{\psi(y)}\frac{\partial^2\psi(y)}{\partial y^2} = E \quad -(3)$$

If we write $E = E_x + E_y$, then

$$\underbrace{-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} = E_x}_{x\text{-dependent}} \qquad \underbrace{-\frac{\hbar^2}{2m}\frac{1}{\psi(y)}\frac{\partial^2\psi(y)}{\partial y^2} = E_y}_{y\text{-dependent}}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E_x\,\psi(x) \qquad -\frac{\hbar^2}{2m}\frac{d^2\psi(y)}{dy^2} = E_y\,\psi(y)$$

The solutions to these differential equation are

$$\psi(x) = A_x \sin\left(\frac{n_x\pi x}{L}\right) \quad \text{and} \quad \psi(y) = A_y \sin\left(\frac{n_y\pi y}{L}\right)$$

$$\Psi(x,y) = A_x A_y \sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)$$

And, the energies are,

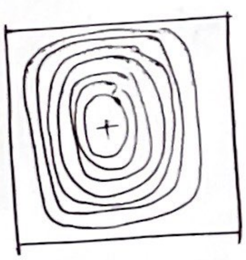
$$E_x = \frac{n_x^2 h^2}{8mL_x^2} \quad \text{and} \quad E_y = \frac{n_y^2 h^2}{8mL_y^2}$$

Total energy $E = E_x + E_y$

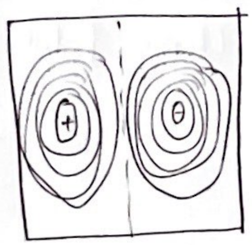
$$E = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right]$$

Degeneracy: If $L_x = L_y$, the wave functions $\psi_{1,2}$ and $\psi_{2,1}$ will correspond to the same energies. We say that $\psi_{1,2}$ and $\psi_{2,1}$ are degenerate.

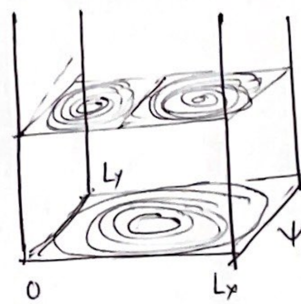
$$E = \frac{h^2}{8mL^2}(n_x^2 + n_y^2) \approx (1^2+2^2)\frac{h^2}{8mL^2}$$
$$\approx (2^2+1^2)\frac{h^2}{8mL^2}$$

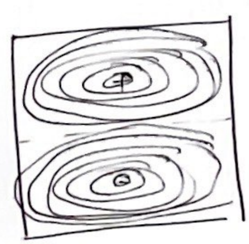


$\psi_{1,1}$



$\psi_{1,2}$





$\psi_{2,1}$

⇒ Particle in 3-D box

Similarly we can write for a particle in a 3-D box

$$\Psi_{n_x n_y n_z} = A_x A_y A_z \sin\frac{n_x \pi x}{L} \sin\frac{n_y \pi y}{L} \sin\frac{n_z \pi z}{L}$$

and the energy,

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

$n_x = 1, 2, 3 \ldots$

$n_y = 1, 2, 3 \ldots$

$n_z = 1, 2, 3 \ldots$

⊛ Read degeneracy

$L_x = L_y = L_z$

$$E = \frac{9h^2}{8mL^2}$$

$n_x^2 + n_y^2 + n_z^2 = 9$

$(1,2,2)\ (2,1,2)\ (2,2,1)$

Three fold degenerate.