Operators

Operators are simply mathematical tools that operate on a function to produce another or same function.

In other words, an operator is a "rule" that transforms a given function into another function

$$\hat{A}f(x) = g(x)$$

A 'caret' is used to designate an operator

Example: $\hat{A} \equiv \frac{d}{dx}$ and $f(x) = x^2$

$$\hat{A}f(x) = \frac{dx^2}{dx} = 2x = \frac{2}{x}f(x)$$

Operators corresponding to observables:

$\widehat{x} = x \times$ [Position operator]

$\hat{p}_x = -i\hbar\frac{d}{dx}$ [Linear momentum operator]

$\widehat{K} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ [Kinetic energy operator]

$\widehat{V} = \frac{1}{2}kx^2 \times$ [Potential energy (harmonic) operator]

Exercise: Apply the following operators on the given functions:

(i) Operator $\hat{p}_x = -i\hbar\frac{d}{dx}$ and functions $exp(-ikx)$ & $exp(ikx)$

(ii) Operator $\widehat{K} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ and functions $exp(-ikx)$ & $exp(ikx)$

Linear Operators

A linear operator satisfies the following relation:

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

c_1 and c_2 are constants and can be complex numbers

Examples of Linear Operators:

(i) Differentiation:

$$\frac{d}{dx}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \frac{df_1(x)}{dx} + c_2 \frac{df_2(x)}{dx}$$

(ii) Integration:

$$\int [c_1 f_1(x) + c_2 f_2(x)]\, dx = c_1 \int f_1(x)\, dx + c_2 \int f_2(x)\, dx$$

Exercise: $\hat{A} \equiv x^2$

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = x^2[c_1 f_1(x) + c_2 f_2(x)]$$
$$= [c_1 x^2 f_1(x) + c_2 x^2 f_2(x)]$$
$$= c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

Exercise: $\hat{A} \equiv SQRT \equiv \sqrt{}$ [Nonlinear operator]

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = \sqrt{[c_1 f_1(x) + c_2 f_2(x)]}$$
$$\neq [c_1 \sqrt{f_1(x)} + c_2 \sqrt{f_2(x)}]$$

Hermitian operators satisfy an eigenfunction-eigenvalue equation

$$\hat{A}f(x) = af(x)$$

Eigenvalue, has to be real constant
$(a = a^*)$

Eigenfunction

(Operator)(function) = (constant factor)(same function)

(Operator corresponding to an observable) ψ **= (value of the observable)** ψ

(Energy operator) ψ **= (energy)** ψ

Examples:

(i) $\hat{A} \equiv \frac{d}{dx}$ and $f(x) = e^{ax^2}$

$$\frac{d(e^{ax^2})}{dx} = 2a(xe^{ax^2}) = 2axf(x)$$

⇒ **This is not an eigenfunction-eigenvalue equation**

⇒ $\hat{A}$ **and** e^{ax} **do not satisfy eigenfunction-eigenvalue relationship**

(ii) $\hat{A} = \frac{d^2}{dx^2}$ and $f(x) = \sin ax$

$$\frac{d^2}{dx^2}(\sin a\, x) = -a^2 \sin ax$$

⇒ **This is an eigenfunction-eigenvalue relationship, the eigenvalue is** $-a^2$

Hermitian Operators

All quantum mechanical operators corresponding to an observable are Hermitian.

- This is because the only possible values of an observable are the eigenvalues of the corresponding operator.
- This means that the eigenvalue must be real.
- This requirement is fulfilled by a Hermitian operator

A Hermitian operator can itself be complex and it must satisfy the following condition

$$\int_{all\ space} \psi^* \hat{A}\phi d\tau = \int_{all\ space} \phi(\hat{A}\psi)^* d\tau$$

$(\hat{A}\psi)^*$ is complex conjugate of $(\hat{A}\psi)$

When $\psi = \phi$

$$\int_{all\ space} \psi^* \hat{A}\psi d\tau = \int_{all\ space} \psi(\hat{A}\psi)^* d\tau$$

If ψ and ϕ are replaced with eigenvalues of $\hat{A}$ ($\hat{A}\psi_n = a_n\psi_n$), then

$$\int_{all\ space} \psi_n^* \hat{A}\psi_m d\tau = \int_{all\ space} \psi_m(\hat{A}\psi_n)^* d\tau$$

$(\hat{A}\psi_n)^*$ is complex conjugate of $(\hat{A}\psi_n)$

More about Hermitian operator…

$(i)\ \hat{A} \equiv \frac{d}{dx} \quad (ii)\ \hat{p}_x \equiv -i\hbar\frac{d}{dx} \quad (iii)\ \hat{K} \equiv -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

$$(i)\quad \int_{-\infty}^{\infty} f^*\frac{d}{dx}f\,dx = \int_{-\infty}^{\infty} f^*\frac{df}{dx}dx = f^*f\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f\frac{df^*}{dx}dx$$

If f is a well − behaved function just as wavefunction,
then $f(x=-\infty) = f(x=\infty) = f^*(x=-\infty) = f^*(x=\infty) = 0$

$$\Rightarrow \int_{-\infty}^{\infty} f^*\frac{d}{dx}f\,dx = -\int_{-\infty}^{\infty} f\frac{df^*}{dx}dx$$

$\Rightarrow \frac{d}{dx}$ *is not Hermitian*

$$(ii)\quad \int_{-\infty}^{\infty} f^*\hat{p}_x f\,dx = \int_{-\infty}^{\infty} f^*\left(-i\hbar\frac{d}{dx}\right)f\,dx = -i\hbar\int_{-\infty}^{\infty} f^*\frac{df}{dx}dx$$

$$= -i\hbar\left[f^*f\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} ff^*dx\right]$$

If f is a well − behaved function just as wavefunction,
then $f(x=-\infty) = f(x=\infty) = f^*(x=-\infty) = f^*(x=\infty) = 0$

$$\Rightarrow \int_{-\infty}^{\infty} f^*\hat{p}_x f\,dx = i\hbar\int_{-\infty}^{\infty} f\frac{df^*}{dx}dx$$

Similarly, $\int_{-\infty}^{\infty} f(\hat{p}_x f)^*dx = \int_{-\infty}^{\infty} f\left(-i\hbar\frac{df}{dx}\right)^* dx = i\hbar\int_{-\infty}^{\infty} f\frac{df^*}{dx}dx$

$\Rightarrow \hat{p}_x = -i\hbar\frac{d}{dx}$ *is Hermitian*

$$(iii)\quad \int_{-\infty}^{\infty} f^*\hat{K}f\,dx = \int_{-\infty}^{\infty} f^*\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)f\,dx$$

$$= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} f^*\frac{d^2f}{dx^2}dx$$

$$= -\frac{\hbar^2}{2m}\left[f^*\frac{df}{dx}\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\frac{df^*}{dx}\frac{df}{dx}dx\right]$$

$$= \frac{\hbar^2}{2m}\left[\frac{df^*}{dx}f\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\frac{d^2f^*}{dx^2}f\,dx\right]$$

$$= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\frac{d^2f^*}{dx^2}f\,dx$$

and, $\int_{-\infty}^{\infty} f(\hat{K}f)^*dx = \int_{-\infty}^{\infty} f\left(-\frac{\hbar^2}{2m}\frac{d^2f^*}{dx^2}\right)dx$

$\Rightarrow \hat{K} =- -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ *is Hermitian*

Eigenfunctions of a Hermitian operator form an orthonormal set

Ortho-normality Condition: Eigenfunctions of a Hermitian operator satisfy following orthonormality condition

$$\int_{all\ space} \psi_m^* \psi_n \, d\tau = \delta_{mn}$$

Kronecker Delta

$$\delta_{mn} = 0 \text{ when } m \neq n$$
$$= 1 \text{ when } m = n$$

Consider $\hat{A}\psi_n = a_n\psi_n$ and $\hat{A}\psi_m = a_m\psi_m$

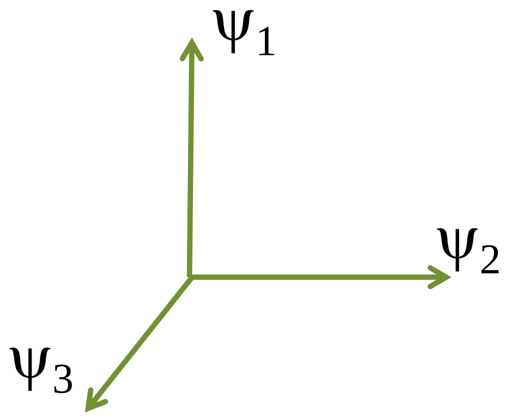
$$\int_{-\infty}^{\infty} \psi_m^* \hat{A}\psi_n dx = \int_{-\infty}^{\infty} \psi_m^* (a_n\psi_n) dx = a_n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx$$

$$\int_{-\infty}^{\infty} \psi_n (\hat{A}\psi_m)^* dx = \int_{-\infty}^{\infty} \psi_n (a_m\psi_m)^* dx = a_m{}^* \int_{-\infty}^{\infty} \psi_n \psi_m^* dx = a_m{}^* \int_{-\infty}^{\infty} \psi_m^* \psi_n dx$$

$$\Rightarrow \int_{-\infty}^{\infty} \psi_m^* \hat{A}\psi_n dx - \int_{-\infty}^{\infty} \psi_n (\hat{A}\psi_m)^* dx = (a_n - a_m{}^*) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx$$

As $\hat{A}$ is Hermitian, the LHS is zero, hence $(a_n - a_m{}^*) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0$

In other words, we can say that the wavefunctions corresponding to different energies are orthogonal



$\Rightarrow$ For $m = n$, $\int_{-\infty}^{\infty} \psi_n^* \psi_n dx = 1$ $(Normalization)$

$\Rightarrow$ $a_n = a_n{}^*$

$\Rightarrow$ For $m \neq n$ $(a_n - a_m{}^*) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0.$

If the system is nondegenerate, $a_n \neq a_m{}^* = a_m$

$\Rightarrow \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad for \quad m \neq n$

Eigenfunctions of a Hermitian operator form an orthonormal set

Example: Orthonormalty of wavefunctions of a particle in a box

$$\psi_n(x) = \sqrt{\left(\frac{2}{L}\right)} Sin\left(\frac{n\pi x}{L}\right) \quad \text{for} \quad 0 \leq x \leq L$$

We can verify the **orthogonality of wavefunctions of a particle in a box** with $n = 1$ and $n = 3$

$$\int_0^L \psi_1^* \psi_1 dx = \frac{2}{L}\int_0^L \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right) dx = 1$$

$$\int_0^L \psi_3^* \psi_3 dx = \frac{2}{L}\int_0^L \sin\left(\frac{3\pi x}{L}\right)\sin\left(\frac{3\pi x}{L}\right) dx = 1$$

$$\int_0^L \psi_1^* \psi_3 dx = \frac{2}{L}\int_0^L \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{3\pi x}{L}\right) dx = 0$$

Expectation Value and Superposition

- **In most cases,** ψ is not an eigenfunction of $\hat{A}$. Then average value of an observable A is calculated as

$$\langle a \rangle = \frac{\int_{volume} \psi^*(\boldsymbol{r})\hat{A}_{observable}\psi(\boldsymbol{r})d\boldsymbol{r}}{\int_{volume} \psi^*(\boldsymbol{r})\psi(\boldsymbol{r})d\boldsymbol{r}} = \int_{volume} \psi^*_{norm}(\boldsymbol{r})\hat{A}_{observable}\psi_{norm}(\boldsymbol{r})d\boldsymbol{r}$$

When the wave function ψ is normalized $\int \psi^*(\boldsymbol{r})\psi(\boldsymbol{r})d\boldsymbol{r} = 1$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} \psi^*(x)\hat{x}\psi(x)dx}{\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx} = \int_{-\infty}^{\infty} \psi^*_{normalized}(x)x\psi_{normalized}(x)dx$$

$$\langle p_x \rangle = \frac{\int_{-\infty}^{\infty} \psi^*(x)\hat{p}_x\psi(x)dx}{\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx} = \int_{-\infty}^{\infty} \psi^*_{normalized}(x)(-i\hbar)\frac{\partial}{\partial x}\psi_{normalized}(x)dx$$

$$\langle E \rangle = \frac{\int_{-\infty}^{\infty} \psi^*(x)\hat{H}\psi(x)dx}{\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx}$$

$$= \int_{-\infty}^{\infty} \psi^*_{normalized}(x)(\hat{K} + \hat{V})\psi_{normalized}(x)dx$$

$$= \int_{-\infty}^{\infty} \psi^*_{normalized}(x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}\right)\psi_{normalized}(x)dx$$

However, if $\{\phi_n\}$ are the set of eigenfunctions of the operator $\hat{A}$ with corresponding eigenvalue as a_n, then we can write ψ as a linear superposition of the eigenfunctions of $\hat{A}$.

$\psi = \sum_n c_n \phi_n$; c_n are constants

Expectation Values and Superposition

$$\psi = \sum_n c_n \phi_n$$

As ϕ_n are orthonormal, ψ has to be normalized

$$\Rightarrow \int_{All\ space} \psi^* \psi d\tau = 1$$

$$\Rightarrow \int_{All\ space} \left(\sum_n c_n \phi_n\right)^* \left(\sum_m c_m \phi_m\right) d\tau = 1$$

$$\Rightarrow \sum_n c_n^* c_n \int_{All\ space} \phi_n^* \phi_n d\tau = 1$$

$$\Rightarrow \sum_n c_n^* c_n = \sum_n |c_n|^2 = 1$$

The average value of observable A is given by

$$\langle a \rangle = \int_{All\ space} \left(\sum_n c_n \phi_n\right)^* \hat{A} \left(\sum_m c_m \phi_m\right) d\tau$$

$$= \sum_{n,m} c_n^* c_m \int_{All\ space} \phi_n^* \hat{A} \phi_m d\tau$$

$$= \sum_{n,m} c_n^* c_m \int_{All\ space} \phi_n^* a_m \phi_m d\tau$$

$$= \sum_{n,m} c_n^* c_m a_m \int_{All\ space} \phi_n^* \phi_m d\tau$$

$$= \sum_n |c_n|^2 a_n$$

$\Rightarrow$ The average value $\langle a \rangle$ is the sum of the possible measured values (a_n) weighted by nonnegative coefficients $|c_n|^2$, which can be interpreted as the probability of measuring the value a_n.

Expectation Values and Superposition

$$\psi = \sum_n c_n \phi_n$$

The value of c_n can be calculated as follows:

⇒ $$\int_{All\ space} {\phi_m}^* \psi d\tau = \int_{All\ space} {\phi_m}^* \sum_n c_n \phi_n \, d\tau = c_m$$

⇒ Therefore, the probability of measuring the eigenvalue a_n is given by

$$|c_m|^2 = \left| \int_{All\ space} {\phi_m}^* \psi d\tau \right|^2$$