Quantum Mechanics I

PHY 3103

Dr. Mohammad Abdur Rashid

Hermiticity of operators in Quantum Mechanics

Wave function and Schrödinger equation

The wave function $\Psi(x,t)$ that describes the quantum mechanics of a particle of mass m moving in a potential $V(x,t)$ satisfies the Schrödinger equation

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

Operators

Every observable in quantum mechanics is represented by a linear, Hermitian operator.

$$\hat{x} = x$$

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

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

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

$$\hat{\Omega}\Psi(x) = \omega\Psi(x)$$

Linear operator

$$\hat{A}(a\phi) \equiv a\hat{A}\phi$$

$$\hat{A}(\phi_1 + \phi_2) \equiv \hat{A}\phi_1 + \hat{A}\phi_2$$

$$(\hat{A} + \hat{B})\phi \equiv \hat{A}\phi + \hat{B}\phi$$

$$\hat{A}\hat{B}\phi \equiv \hat{A}(\hat{B}\phi)$$

Hermitian operator

An operator $\hat{\Omega}$, which corresponds to a physical observable Ω, is said to be Hermitian if

$$\boxed{\int \Phi^* \hat{\Omega} \Psi \, \mathrm{d}x = \int (\hat{\Omega}\Phi)^* \Psi \, \mathrm{d}x}$$

Briefer notation

The integrals of pairs of functions:

$$(\Phi, \Psi) = \int \Phi^*(x)\Psi(x)\,\mathrm{d}x$$

For any complex constant *a*:

$$(a\Phi, \Psi) = a^*(\Phi, \Psi)$$

$$(\Phi, a\Psi) = a(\Phi, \Psi)$$

Hermitian operator

Hermitian: $$(\Phi, \hat{\Omega}\Psi) = (\hat{\Omega}\Phi, \Psi)$$

Anti-Hermitian: $$(\Phi, \hat{\Omega}\Psi) = -(\hat{\Omega}\Phi, \Psi)$$

Properties of Hermitian operator

- The expectation value of a Hermitian operator is real.
- The eigenvalues of a Hermitian operator are real.
- The eigenfunctions can be organized to satisfy orthonormality.
- The eigenfunctions of Hermitian operator form a complete set of basis functions. Any reasonable wave function can be written as a superposition of eigenfunctions of that operator.

Real expectation value for Hermitian operator

The expectation value of Ω is defined as

$$\langle \Omega \rangle_\Psi = \int \Psi^*(x)\,\hat{\Omega}\Psi(x)\,\mathrm{d}x = (\Psi, \hat{\Omega}\Psi)$$

The complex conjugate

$$(\langle \Omega \rangle_\Psi)^* = \int (\Psi^*\,\hat{\Omega}\Psi)^*\,\mathrm{d}x = \int \Psi(\hat{\Omega}\Psi)^*\,\mathrm{d}x$$

Real expectation value for Hermitian operator

$$\left(\langle \Omega \rangle_{\Psi}\right)^{*} = \int (\hat{\Omega}\Psi)^{*}\, \Psi \, \mathrm{d}x$$

$$= \int \Psi^{*}\, \hat{\Omega}\Psi \, \mathrm{d}x$$

$$= \langle \Omega \rangle_{\Psi}$$

$$Z = A + iB$$

$$Z^{*} = A - iB$$

The expectation value of a Hermitian operator is real.

Properties of Hermitian operator

- The expectation value of a Hermitian operator is real.
- The eigenvalues of a Hermitian operator are real.
- The eigenfunctions can be organized to satisfy orthonormality.
- The eigenfunctions of Hermitian operator form a complete set of basis functions. Any reasonable wave function can be written as a superposition of eigenfunctions of that operator.

Real eigenvalues for Hermitian operator

Assume the operator $\hat{\Omega}$ has an eigenvalue ω associated with a normalized eigenfunction $\Psi(x)$:

$$\hat{\Omega}\Psi(x) = \omega\Psi(x)$$

The expectation value of $\hat{\Omega}$ in the state of $\Psi(x)$:

$$\langle\Omega\rangle_{\Psi} = (\Psi, \hat{\Omega}\Psi) = (\Psi, \omega\Psi) = \omega(\Psi, \Psi) = \omega$$

The eigenvalues of a Hermitian operator are real.

Properties of Hermitian operator

- The expectation value of a Hermitian operator is real.
- The eigenvalues of a Hermitian operator are real.
- The eigenfunctions can be organized to satisfy orthonormality.
- The eigenfunctions of Hermitian operator form a complete set of basis functions. Any reasonable wave function can be written as a superposition of eigenfunctions of that operator.

Orthonormal eigenfunctions for Hermitian operator

Assume that the Hermitian operator $\hat{\Omega}$ has a collection of eigenfunctions and eigenvalues:

$$\begin{aligned}
\hat{\Omega}\psi_1(x) &= \omega_1\psi_1(x) \\
\hat{\Omega}\psi_2(x) &= \omega_2\psi_1(x) \\
\hat{\Omega}\psi_3(x) &= \omega_3\psi_1(x) \\
&\vdots
\end{aligned}$$

The list may be finite or infinite.

Orthonormal eigenfunctions for Hermitian operator

$$(\psi_i, \psi_j) = \int \psi_i^*(x)\, \psi_j(x)\, \mathrm{d}x = \delta_{ij}$$

The Kronecker delta: $$\delta_{ij} = \begin{cases} 1 & \text{if} \quad i = j, \\ 0 & \text{if} \quad i \neq j. \end{cases}$$

Orthonormal eigenfunctions for Hermitian operator

We evaluate $(\psi_i, \hat{\Omega}\psi_j)$ in two different ways.

$$\begin{aligned}(\psi_i, \hat{\Omega}\psi_j) &= (\psi_i, \omega_j \psi_j) \\ &= \omega_j (\psi_i, \psi_j)\end{aligned}$$

$$\omega_i \neq \omega_j$$

$$\begin{aligned}\hat{\Omega}\psi_1(x) &= \omega_1 \psi_1(x) \\ \hat{\Omega}\psi_2(x) &= \omega_2 \psi_1(x) \\ \hat{\Omega}\psi_3(x) &= \omega_3 \psi_1(x) \\ &\vdots\end{aligned}$$

Orthonormal eigenfunctions for Hermitian operator

$$
\begin{aligned}
(\psi_i, \hat{\Omega}\psi_j) &= (\hat{\Omega}\psi_i, \psi_j) \\
&= (\omega_i\psi_i, \psi_j) \\
&= \omega_i^*(\psi_i, \psi_j) \\
&= \omega_i(\psi_i, \psi_j)
\end{aligned}
$$

$$\omega_i \neq \omega_j$$

$$
\begin{aligned}
\hat{\Omega}\psi_1(x) &= \omega_1\psi_1(x) \\
\hat{\Omega}\psi_2(x) &= \omega_2\psi_1(x) \\
\hat{\Omega}\psi_3(x) &= \omega_3\psi_1(x) \\
&\vdots
\end{aligned}
$$

Orthonormal eigenfunctions for Hermitian operator

$$(\omega_j - \omega_i)(\psi_i,\ \psi_j) = 0$$

$$(\psi_i, \psi_j) = \int \psi_i^*(x)\, \psi_j(x)\, \mathrm{d}x = \delta_{ij}$$

The eigenfunctions of a Hermitian operator can be organized to satisfy orthonormality.

Orthonormal eigenfunctions for Hermitian operator

$$(\psi_i, \psi_j) = \int \psi_i^*(x)\, \psi_j(x)\, \mathrm{d}x = \delta_{ij}$$

It is possible to have degeneracies in the spectrum, namely, different eigenfunctions with the same eigenvalue. In that case one must show that it is possible to choose linear combinations of the degenerate eigenfunctions that are mutually orthogonal.

Properties of Hermitian operator

- The expectation value of a Hermitian operator is real.
- The eigenvalues of a Hermitian operator are real.
- The eigenfunctions can be organized to satisfy orthonormality.
- The eigenfunctions of Hermitian operator form a complete set of basis functions. Any reasonable wave function can be written as a superposition of eigenfunctions of that operator.

A complete set of basis functions for Hermitian operator

The eigenfunctions of $\hat{\Omega}$ form a complete set of basis functions. Any reasonable Ψ can be written as a superposition of eigenfunctions of $\hat{\Omega}$.

$$\Psi(x) = \alpha_1\psi_1(x) + \alpha_2\psi_2(x) + \cdots = \sum_i \alpha_i\psi_i(x)$$

$$\alpha_i = (\psi_i,\ \Psi)$$

A complete set of basis functions for Hermitian operator

$$
\begin{aligned}
(\psi_i,\ \Psi) &= \int \psi_i^*(x)\,\Psi(x) \\
&= \int \psi_i^*(x) \sum_j \alpha_j \psi_j(x)\,\mathrm{d}x \\
&= \sum_j \alpha_j \int \psi_i^*(x)\,\psi_j(x)\,\mathrm{d}x \\
&= \sum_j \alpha_j \delta_{ij} = \alpha_i
\end{aligned}
$$

Hermitian operator

An operator $\hat{\Omega}$, which corresponds to a physical observable Ω, is said to be Hermitian if

$$\int \Phi^* \hat{\Omega} \Psi \, \mathrm{d}x = \int (\hat{\Omega}\Phi)^* \Psi \, \mathrm{d}x$$

Properties of Hermitian operator

- The expectation value of a Hermitian operator is real.
- The eigenvalues of a Hermitian operator are real.
- The eigenfunctions can be organized to satisfy orthonormality.
- The eigenfunctions of Hermitian operator form a complete set of basis functions. Any reasonable wave function can be written as a superposition of eigenfunctions of that operator.

Examples of Hermitian operator

Hermitian operator

An operator $\hat{\Omega}$, which corresponds to a physical observable Ω, is said to be Hermitian if

$$\int \Phi^* \hat{\Omega} \Psi \, \mathrm{d}x = \int (\hat{\Omega} \Phi)^* \Psi \, \mathrm{d}x$$

Properties of Hermitian operator

- The expectation value of a Hermitian operator is real.
- The eigenvalues of a Hermitian operator are real.
- The eigenfunctions can be organized to satisfy orthonormality.
- The eigenfunctions of Hermitian operator form a complete set of basis functions. Any reasonable wave function can be written as a superposition of eigenfunctions of that operator.

Operators

Every observable in quantum mechanics is represented by a linear, Hermitian operator.

$$\hat{x} = x$$

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

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

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

$$\hat{\Omega}\Psi(x) = \omega\Psi(x)$$

Briefer notation

The integrals of pairs of functions:

$$(\Phi, \Psi) = \int \Phi^*(x)\Psi(x)\,\mathrm{d}x$$

For any complex constant *a*:

$$(a\Phi, \Psi) = a^*(\Phi, \Psi)$$

$$(\Phi, a\Psi) = a(\Phi, \Psi)$$

Hermitian operator

Hermitian: $$\boxed{(\Phi, \hat{\Omega}\Psi) = (\hat{\Omega}\Phi, \Psi)}$$

Anti-Hermitian: $$\boxed{(\Phi, \hat{\Omega}\Psi) = -(\hat{\Omega}\Phi, \Psi)}$$

Position operator

01: Position operator $\hat{x}$ is a Hermitian operator.

$$
\begin{aligned}
(\Phi,\, \hat{x}\Psi) &= \int \Phi^*(x)\big(\hat{x}\Psi(x)\big)\,\mathrm{d}x \\
&= \int \Phi^*(x)\big(x\Psi(x)\big)\,\mathrm{d}x \\
&= \int \big(x\Phi^*(x)\big)\Psi(x)\,\mathrm{d}x
\end{aligned}
$$

$$
\hat{x}\Phi(x) = x\Phi(x)
$$
$$
\hat{x}\Psi(x) = x\Psi(x)
$$

Position operator

$$
\begin{aligned}
(\Phi,\ \hat{x}\Psi) &= \int (x\Phi(x))^* \, \Psi(x) \, \mathrm{d}x \\
&= \int (\hat{x}\Phi(x))^* \, \Psi(x) \, \mathrm{d}x \\
&= (\hat{x}\Phi,\ \Psi)
\end{aligned}
$$

$$
\hat{x}\Phi(x) = x\Phi(x)
$$
$$
\hat{x}\Psi(x) = x\Psi(x)
$$

Position operator $\hat{x}$ is a Hermitian operator.

Momentum operator

02: Momentum operator $\hat{p}$ is a Hermitian operator.

$$\begin{aligned}(\Phi, \hat{p}\Psi) &= \int \Phi^*(x)\left(\hat{p}\Psi(x)\right)\mathrm{d}x \\ &= \int \Phi^*(x)\,(-i\hbar)\frac{\partial\Psi(x)}{\partial x}\,\mathrm{d}x \\ &= -i\hbar\int \Phi^*(x)\,\frac{\partial\Psi(x)}{\partial x}\,\mathrm{d}x\end{aligned}$$

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

Momentum operator

Integrating by parts we have

$$
\begin{aligned}
(\Phi,\, \hat{p}\Psi) &= -i\hbar \int \Phi^*(x)\,\frac{\partial \Psi(x)}{\partial x}\,\mathrm{d}x \\
&= -i\hbar\Big[\Phi^*(x)\Psi(x)\Big]_{-\infty}^{\infty} - (-i\hbar)\int \frac{\partial \Phi^*(x)}{\partial x}\,\Psi(x)\,\mathrm{d}x
\end{aligned}
$$

Since the wave function vanishes as $x \to \pm\infty$ the first term in the right-hand side is zero.

Momentum operator

$$
\begin{aligned}
(\Phi,\, \hat{p}\Psi) &= i\hbar \int \frac{\partial \Phi^*(x)}{\partial x}\, \Psi(x)\, \mathrm{d}x \\
&= \int \left(-i\hbar \frac{\partial \Phi(x)}{\partial x} \right)^* \Psi(x)\, \mathrm{d}x \\
&= \int \left(\hat{p}\Phi(x) \right)^* \Psi(x)\, \mathrm{d}x \\
&= (\hat{p}\Phi,\, \Psi)
\end{aligned}
$$

Momentum operator $\hat{p}$ is a Hermitian operator.

Hermitian operator

$$\frac{\partial}{\partial x} \text{ is an anti-Hermitian operator.}$$

$$\frac{\partial^2}{\partial x^2} \text{ is a Hermitian operator.}$$

Time dependence of expectation values

Schrödinger Equation

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

For a particle quantum mechanical of mass m moving in a potential $V(x,t)$ the Hamiltonian operator is

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

Hermitian operator

An operator $\hat{\Omega}$, which corresponds to a physical observable Ω, is said to be Hermitian if

$$\boxed{\int \Phi^* \hat{\Omega} \Psi \, \mathrm{d}x = \int (\hat{\Omega}\Phi)^* \Psi \, \mathrm{d}x}$$

Examples: position operator $\hat{x}$, momentum operator $\hat{p}$, Hamiltonian operator $\hat{H}$, etc.

Expectation value

The expectation value $\langle \Omega \rangle$ of any operator $\hat{\Omega}$:

$$\boxed{\langle \Omega \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\, \hat{\Omega} \Psi(x,t)\, \mathrm{d}x}$$

The physical meaning of this would be if we consider many copies of the identical system, and measure Ω at a time t in all of them, then the average value recorded will converge to $\langle \Omega \rangle$ as the number of systems and measurements approaches infinity.

Time dependence of expectation values

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\langle\Omega\rangle = i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty}\Psi^*(x,t)\,\hat{\Omega}\Psi(x,t)\,\mathrm{d}x$$

$$= i\hbar\int_{-\infty}^{\infty}\left(\frac{\partial\Psi^*}{\partial t}\,\hat{\Omega}\Psi + \Psi^*\,\hat{\Omega}\frac{\partial\Psi}{\partial t}\right)\mathrm{d}x$$

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

$$-i\hbar\frac{\partial\Psi^*}{\partial t} = \left(\hat{H}\Psi\right)^*$$

Time dependence of expectation values

$$
\begin{aligned}
i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\langle\Omega\rangle &= \int_{-\infty}^{\infty}\left\{-(\hat{H}\Psi)^*\,\hat{\Omega}\Psi + \Psi^*\,\hat{\Omega}(\hat{H}\Psi)\right\}\mathrm{d}x \\
&= \int_{-\infty}^{\infty}\left\{\Psi^*\,\hat{\Omega}(\hat{H}\Psi) - (\hat{H}\Psi)^*\,\hat{\Omega}\Psi\right\}\mathrm{d}x
\end{aligned}
$$

Hermitian operator: $\boxed{\int \Phi^*\hat{\Omega}\Psi\,\mathrm{d}x = \int (\hat{\Omega}\Phi)^*\Psi\,\mathrm{d}x}$

Time dependence of expectation values

$$
\begin{aligned}
i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\langle\Omega\rangle &= \int_{-\infty}^{\infty}\left(\Psi^*\,\hat{\Omega}\hat{H}\Psi - \Psi^*\,\hat{H}\hat{\Omega}\Psi\right)\mathrm{d}x \\
&= \int_{-\infty}^{\infty}\Psi^*(\hat{\Omega}\hat{H} - \hat{H}\hat{\Omega})\Psi\,\mathrm{d}x \\
&= \int_{-\infty}^{\infty}\Psi^*[\hat{\Omega},\ \hat{H}]\Psi\,\mathrm{d}x
\end{aligned}
$$

Commutator of two operators:

$$\boxed{[\hat{A},\hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}}$$

Time dependence of expectation values

We have proven that for operators $\hat{\Omega}$ that do not explicitly depend on time,

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t}\langle \Omega \rangle = \left\langle [\hat{\Omega},\ \hat{H}] \right\rangle$$

Therefore, for an operation which commute with the Hamiltonian operator $\hat{H}$ the expectation value will not change over time.

Time dependence of expectation values

Example: Consider the momentum operator $\hat{p}$ for a free particle.

For a free particle the Hamiltonian operator: $\hat{H} = \dfrac{\hat{p}^2}{2m}$

Time dependence of expectation values

Hence the momentum operator $\hat{p}$ commute with $\hat{H}$:

$$[\hat{p},\ \hat{H}] = [\hat{p},\ \frac{\hat{p}^2}{2m}] = \frac{1}{2m}[\hat{p},\ \hat{p}^2]$$
$$= \frac{1}{2m}\Big([\hat{p},\ \hat{p}]\hat{p} + \hat{p}[\hat{p},\ \hat{p}]\Big) = 0$$

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$$

Time dependence of expectation values

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t}\langle p\rangle = \left\langle [\hat{p},\ \hat{H}] \right\rangle = 0$$

For a free particle the expectation value of momentum does not change over time.