Consideration of the quantum mechanical description of the particle-in-a-box exposed two important properties of quantum mechanical systems. We saw that the eigenfunctions of the Hamiltonian operator are orthogonal, and we also saw that the position and momentum of the particle could not be determined exactly. We now examine the generality of these insights by stating and proving some fundamental theorems. These theorems use the Hermitian property of quantum mechanical operators, which is described first.

Hermitian Operators

Since the eigenvalues of a quantum mechanical operator correspond to measurable quantities, the eigenvalues must be real, and consequently a quantum mechanical operator must be Hermitian. To prove this, we start with the premises that \(\langle \psi \rangle\) and \(\langle \phi \rangle\) are functions, \(\int d\tau\) represents integration over all coordinates, and the operator \(\hat{A}\) is Hermitian by definition if

\[
\int \psi^* \hat{A} \psi \,d\tau = \int (\hat{A}^* \psi^*) \psi \,d\tau \label{4-37}\]

This equation means that the complex conjugate of \(\hat{A}\) can operate on \(\psi^*\) to produce the same result after integration as \(\hat{A}\) operating on \(\phi\), followed by integration. To prove that a quantum mechanical operator \(\hat{A}\) is Hermitian, consider the eigenvalue equation and its complex conjugate.

\[
\hat{A} \psi = a \psi \label{4-38}\]
\[
\hat{A}^* \psi^* = a^* \psi^* = a \psi^* \label{4-39}\]

Note that \(a^* = a\) because the eigenvalue is real. Multiply Equation \(\ref{4-38}\) and \(\ref{4-39}\) from the left by \(\psi^*\) and \(\psi\), respectively, and integrate over the full range of all the coordinates. Note that \(\psi\) is normalized. The results are

\[
\int \psi^* \hat{A} \psi \,d\tau = a \int \psi^* \psi \,d\tau = a \label{4-40}\]
\[
\int \psi \hat{A}^* \psi^* \,d\tau = a \int \psi \psi^* \,d\tau = a \label{4-41}\]

Since both integrals equal \(a\), they must be equivalent.

\[
\int \psi^* \hat{A} \psi \,d\tau = \int (\hat{A}^* \psi^*) \psi \,d\tau \label{4-42}\]

The operator acting on the function,

\[
\int \psi^* \hat{A} \psi \,d\tau = \int \hat{A}^* \psi^* \,d\tau_* \]

produces a new function. Since functions commute, Equation \(\ref{4-42}\) can be rewritten as

\[
\int \psi^* \hat{A} \psi \,d\tau = \int \langle \hat{A}^* \psi^* \rangle \psi \,d\tau \label{4-43}\]

This equality means that \(\langle \hat{A} \rangle\) is \textit{Hermitian}. 
Orthogonality Theorem

Eigenfunctions of a Hermitian operator are orthogonal if they have different eigenvalues. Because of this theorem, we can identify orthogonal functions easily without having to integrate or conduct an analysis based on symmetry or other considerations.

Proof

\( |ψ\rangle \) and \( |φ\rangle \) are two eigenfunctions of the operator \( \hat{A} \) with real eigenvalues \( (a_1) \) and \( (a_2) \), respectively. Since the eigenvalues are real, \( (a_1)^* = a_1 \) and \( (a_2)^* = a_2 \).

\[\hat{A} |ψ\rangle = a_1 |ψ\rangle \]
\[\hat{A}^* |φ^\ast\rangle = a_2 |φ^\ast\rangle \]

Multiply the first equation by \( |φ^\ast\rangle \) and the second by \( |ψ\rangle \) and integrate.

\[\int |ψ^\ast\rangle \hat{A} |ψ\rangle \, d\tau = a_1 \int |ψ^\ast\rangle |ψ\rangle \, d\tau \]
\[\int |ψ\rangle \hat{A}^* |φ^\ast\rangle \, d\tau = a_2 \int |ψ\rangle |φ^\ast\rangle \, d\tau \]

Subtract the two equations in Equation (4-45) to obtain

\[\int |ψ^\ast\rangle \hat{A} |ψ\rangle \, d\tau - \int |ψ\rangle \hat{A}^* |φ^\ast\rangle \, d\tau = (a_1 - a_2) \int |ψ^\ast\rangle |ψ\rangle \, d\tau \]

The left-hand side of Equation (4-46) is zero because \( \hat{A} \) is Hermitian yielding

\[0 = (a_1 - a_2) \int |ψ^\ast\rangle |ψ\rangle \, d\tau \]

If \( (a_1) \) and \( (a_2) \) are not equal, then the integral must be zero. This result proves that nondegenerate eigenfunctions of the same operator are orthogonal.

\( \square \)

Exercise \( \PageIndex{1} \)

Draw graphs and use them to show that the particle-in-a-box wavefunctions for \( (n = 2) \) and \( (n = 3) \) are orthogonal to each other.

Thus, the eigenstate \( |ψ_{al}\rangle \) is a state which is associated with a unique value of the dynamical variable corresponding to \( \hat{A} \). This unique value is simply the associated eigenvalue. It is easily demonstrated that the eigenvalues of operators associated with experimental measurements are all real.

Two wavefunctions, \( |ψ_1(x)\rangle \) and \( |ψ_2(x)\rangle \), are said to be orthogonal if

\[\int_{-\infty}^{\infty} |ψ_1^\ast(x) \hat{A} \psi_2 | \, dx = 0, \label{4.5.1}\]
Consider two eigenstates of \(\hat{A}\), \(\psi_a(x)\) and \(\psi_{a'}(x)\), which correspond to the two different eigenvalues \(a\) and \(a'\), respectively. Thus,

\[
\hat{A}\psi_a = a \psi_a \label{4.5.2}
\]
\[
\hat{A}\psi_{a'} = a' \psi_{a'} \label{4.5.3}
\]

Multiplying the complex conjugate of the first equation by \(\psi_{a'}(x)\), and the second equation by \(\psi_{a'}^*(x)\), and then integrating over all \(x\), we obtain

\[
\int_{-\infty}^{\infty} (\hat{A} \psi_a)^* \psi_{a'} dx = a \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx, \quad \text{label(4.5.4)}
\]
\[
\int_{-\infty}^{\infty} \psi_a^*(\hat{A} \psi_{a'}) dx = a' \int_{-\infty}^{\infty} \psi_a^* \psi_{a'} dx, \quad \text{label(4.5.5)}
\]

However, from Equation \(\text{ref(4-46)}\), the left-hand sides of the above two equations are equal. Hence, we can write

\[
[(a-a') \int_{-\infty}^{\infty} \psi_{a'}^* \psi_{a'} dx = 0.]
\]

By assumption, \(a \neq a'\), yielding

\[
[\int_{-\infty}^{\infty} \psi_{a'}^* \psi_{a'} dx = 0.]
\]

In other words, eigenstates of an Hermitian operator corresponding to different eigenvalues are automatically orthogonal.

The eigenvalues of operators associated with experimental measurements are all real.

---

**Orthogonality of Degenerate Eigenstates**

Consider two eigenstates of \(\hat{A}\), \(\psi_a\) and \(\psi'_{a}\), which correspond to the same eigenvalue, \(a\). Such eigenstates are termed degenerate. The above proof of the orthogonality of different eigenstates fails for degenerate eigenstates. Note, however, that any linear combination of \(\psi_a\) and \(\psi'_{a}\) is also an eigenstate of \(\hat{A}\) corresponding to the eigenvalue \(a\). Thus, even if \(\psi_a\) and \(\psi'_{a}\) are not orthogonal, we can always choose two linear combinations of these eigenstates which are orthogonal. For instance, if \(\psi_a\) and \(\psi'_{a}\) are properly normalized, and

\[
[\int_{-\infty}^{\infty} \psi_{a'}^* \psi_{a'} dx = c, \text{label(4.5.10)}]
\]

then it is easily demonstrated that

\[
\psi''_a = \frac{\sqrt{1-c}}{\sqrt{1-c^2}} \left( \psi_a - c^{-1} \psi'_{a} \right), \quad \text{label(4.5.11)}
\]

is a properly normalized eigenstate of \(\hat{A}\), corresponding to the eigenvalue \(a\), which is orthogonal to \(\psi_a\). It is straightforward to generalize the above argument to three or more degenerate eigenstates. Hence, we conclude that the eigenstates of an Hermitian operator are, or can be chosen to be, mutually orthogonal.
Theorem: Gram-Schmidt Orthogonalization

If the eigenvalues of two eigenfunctions are the same, then the functions are said to be degenerate, and linear combinations of the degenerate functions can be formed that will be orthogonal to each other. Since the two eigenfunctions have the same eigenvalues, the linear combination also will be an eigenfunction with the same eigenvalue. Degenerate eigenfunctions are not automatically orthogonal, but can be made so mathematically via the Gram-Schmidt Orthogonalization. The proof of this theorem shows us one way to produce orthogonal degenerate functions.

Proof

If \( |ψ\rangle \) and \( |φ\rangle \) are degenerate, but not orthogonal, define \( |Φ\rangle = |φ\rangle - S|ψ\rangle \) where \( S \) is the overlap integral \( \int \psi^* \psi \, dτ \), then \( |ψ\rangle \) and \( |Φ\rangle \) will be orthogonal.

\[
\begin{align*}
\int \psi^* \phi \, dτ &= \int \psi^* (\varphi - S\psi) \, dτ \\
&= \int \psi^* \psi \, dτ - S \int \psi^* \psi \, dτ \\
&= S - S = 0
\end{align*}
\]

\( \square \)

Exercise \( \PageIndex{2} \)

Find \( N \) that normalizes \( |ψ\rangle \) if \( |ψ\rangle = N(φ_1 - Sφ_1) \) where \( |φ_1\rangle \) and \( |φ_2\rangle \) are normalized wavefunctions and \( S \) is their overlap integral.

\( S = \langle φ_1 | φ_2 \rangle \)

We conclude that the eigenstates of an Hermitian operator are, or can be chosen to be, mutually orthogonal.

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