

4.9: Properties of Quantum Mechanical Systems

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 Theorem

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.

Proof

We start with the premises that ψ and ϕ are functions, $\int d\tau$ represents integration over all coordinates, and the operator \hat{A} is Hermitian by definition if

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \quad (4.9.1)$$

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

$$\hat{A} \psi = a \psi \quad (4.9.2)$$

$$\hat{A}^* \psi^* = a^* \psi^* = a \psi^* \quad (4.9.3)$$

Note that $a^* = a$ because the eigenvalue is real. Multiply Equations 4.9.2 and 4.9.3 from the left by ψ^* and ψ , respectively, and integrate over all the coordinates. Note that ψ is normalized. The results are

$$\int \psi^* \hat{A} \psi d\tau = a \int \psi^* \psi d\tau = a \quad (4.9.4)$$

$$\int \psi \hat{A}^* \psi^* d\tau = a \int \psi \psi^* d\tau = a \quad (4.9.5)$$

Since both integrals equal a , they must be equivalent.

$$\int \psi^* \hat{A} \psi d\tau = \int \psi \hat{A}^* \psi^* d\tau \quad (4.9.6)$$

The operator acting on the function, $\hat{A}^* \int \psi^* \hat{A} \psi d\tau = \int \psi \hat{A}^* \psi^* d\tau$, produces a new function. Since functions commute, Equation 4.9.6 can be rewritten as

$$\int \psi^* \hat{A} \psi d\tau = \int (\hat{A}^* \psi^*) \psi d\tau \quad (4.9.7)$$

This equality means that \hat{A} is 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 and ϕ 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 $a_2^* = a_2$.

$$\hat{A} \psi = a_1 \psi \quad (4.9.8)$$

$$\hat{A}^* \psi^* = a_2 \psi^* \quad (4.9.9)$$

Multiply the first equation by ψ^* and the second by ψ and integrate.

$$\int \psi^* \hat{A} \psi d\tau = a_1 \int \psi^* \psi d\tau \quad (4.9.10)$$

$$\int \psi \hat{A}^* \psi^* d\tau = a_2 \int \psi \psi^* d\tau \quad (4.9.11)$$

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

$$\int \psi^* \hat{A} \psi d\tau - \int \psi \hat{A}^* \psi^* d\tau = (a_1 - a_2) \int \psi^* \psi d\tau \quad (4.9.12)$$

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

$$0 = (a_1 - a_2) \int \psi^* \psi d\tau \quad (4.9.13)$$

If a_1 and a_2 in (4-47) are not equal, then the integral must be zero. This result proves that nondegenerate eigenfunctions of the same operator are orthogonal.

Exercise 4.9.44

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.

Schmidt Orthogonalization Theorem

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. The proof of this theorem shows us one way to produce orthogonal degenerate functions.

Proof

If ψ and ϕ are degenerate but not orthogonal, define $\Phi = \phi - S\psi$ where S is the overlap integral $\int \psi^* \psi d\tau$, then ψ and Φ will be orthogonal.

$$\int \psi^* \phi d\tau = \int \psi^* (\phi - S\psi) d\tau = \int \psi^* \phi d\tau - S \int \psi^* \psi d\tau \quad (4.9.14)$$

$$= S - S = 0 \quad (4.9.15)$$

Exercise 4.9.45

Find N that normalizes Φ if $\Phi = N(\phi - S\psi)$ where ψ and ϕ are normalized and S is their overlap integral.

Commuting Operator Theorem

If two operators commute, then they can have the same set of eigenfunctions. By definition, two operators \hat{A} and \hat{B} commute if the effect of applying \hat{A} then \hat{B} is the same as applying \hat{B} then \hat{A} , i.e. $\hat{A}\hat{B} = \hat{B}\hat{A}$. For example, the operations brushing-your-teeth and combing-your-hair commute, while the operations getting-dressed and taking-a-shower do not. This theorem is very important. If two operators commute and consequently have the same set of eigenfunctions, then the corresponding physical quantities can be evaluated or measured exactly simultaneously with no limit on the uncertainty. As mentioned previously, the eigenvalues of the operators correspond to the measured values.

Proof

If \hat{A} and \hat{B} commute and ψ is an eigenfunction of \hat{A} with eigenvalue b , then

$$\hat{B}\hat{A}\psi = \hat{A}\hat{B}\psi = \hat{A}b\psi = b\hat{A}\psi \quad (4.9.16)$$

Equation (4-49) says that $\hat{A}\psi$ is an eigenfunction of \hat{B} with eigenvalue b , which means that when \hat{A} operates on ψ , it cannot change ψ . At most, \hat{A} operating on ψ can produce a constant times ψ .

$$\hat{A}\psi = a\psi \quad (4.9.17)$$

$$\hat{B}(\hat{A}\psi) = \hat{B}(a\psi) = a\hat{B}\psi = ab\psi = b(a\psi) \quad (4.9.18)$$

Equation 4.9.18 shows that Equation 4.9.17 is consistent with Equation 4.9.16. Consequently ψ also is an eigenfunction of \hat{A} with eigenvalue a .

Exercise 4.9.46

Write definitions of the terms orthogonal and commutation.

Exercise 4.9.47

Show that the operators for momentum in the x-direction and momentum in the y-direction commute, but operators for momentum and position along the x-axis do not commute. Since differential operators are involved, you need to show whether

$$\hat{P}_x\hat{P}_y f(x, y) = \hat{P}_y\hat{P}_x f(x, y) \quad (4.9.19)$$

$$\hat{P}_x\hat{x} f(x) = \hat{x}\hat{P}_x f(x) \quad (4.9.20)$$

where f is an arbitrary function, or you could try a specific form for f , e.g. $f = 6xy$.

General Heisenberg Uncertainty Principle

Though it will not be proven here, there is a general statement of the uncertainty principle in terms of the commutation property of operators. If two operators \hat{A} and \hat{B} do not commute, then the uncertainties (standard deviations σ) in the physical quantities associated with these operators must satisfy

$$\sigma_A\sigma_B \geq \left| \int \psi^* [\hat{A}\hat{B} - \hat{B}\hat{A}] \psi d\tau \right| \quad (4.9.21)$$

where the integral inside the square brackets is called the commutator, and $||$ signifies the modulus or absolute value. If \hat{A} and \hat{B} commute, then the right-hand-side of equation (4-52) is zero, so either or both σ_A and σ_B could be zero, and there is no restriction on the uncertainties in the measurements of the eigenvalues a and b . If \hat{A} and \hat{B} do not commute, then the right-hand-side of equation (4-52) will not be zero, and neither σ_A nor σ_B can be zero unless the other is infinite. Consequently, both a and b cannot be eigenvalues of the same wavefunctions and cannot be measured simultaneously to arbitrary precision.

Exercise 4.9.48

Show that the commutator for position and momentum in one dimension equals $-i\hbar$ and that the right-hand-side of Equation (4-52) therefore equals $\hbar/2$ giving $\sigma_x\sigma_{p_x} \geq \frac{\hbar}{2}$

Exercise 4.9.49

In a later chapter you will learn that the operators for the three components of angular momentum along the three directions in space (x, y, z) do not commute. What is the relevance of this mathematical property to measurements of angular momentum in atoms and molecules?

Exercise 4.9.50

Write the definition of a Hermitian operator and statements of the Orthogonality Theorem, the Schmidt Orthogonalization Theorem, and the Commuting Operator Theorem.

Exercise 4.9.51

Reconstruct proofs for the Orthogonality Theorem, the Schmidt Orthogonalization Theorem, and the Commuting Operator Theorem.

Exercise 4.9.52

Write a paragraph summarizing the connection between the commutation property of operators and the uncertainty principle.

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