

# Quantum Mechanics

Week 3

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FS2024

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# 1 Pre-Reading Note

Dear Students,

Welcome to the course on Quantum Mechanics. As part of your learning resources, I will prepare a series of educational materials and sheets designed to complement the lectures.

Please note that these materials are **abridged versions** of the content from the textbook *"Introduction to Quantum Mechanics By David J. Griffiths"*. They have been tailored to align with the class schedule and topics, providing you with concise summaries and key points for each topic covered.

It's important to understand that these sheets are **not standalone resources**. They are intended to be used in conjunction with the class material. For a deeper understanding and a more comprehensive view of each topic, I strongly encourage you to refer to the mentioned textbook.

The book provides detailed explanations, examples, and insights that go beyond the scope of our summaries. It will be an invaluable resource for you to solidify your understanding of Quantum Mechanics.

I cannot guarantee neither correctness nor completeness of the script. Please report any mistake directly to me.

Have fun with Quantum Mechanics!

Best regards,

*Mark Benazet Castells*

## 2 Stationary States in Quantum Mechanics

In quantum mechanics, stationary states are special quantum states of a physical system where the probability density and expectation values of observables do not change over time. These states are significant because they offer a stable and predictable model for understanding quantum systems.

The concept of stationary states becomes particularly relevant when we analyze systems with a time-independent potential,  $V$ . In such systems, the Schrödinger equation, which governs the dynamics of quantum states, simplifies in a way that leads to stationary solutions. The time-independent nature of  $V$  implies that the energy of the system remains constant, which is a characteristic feature of stationary states.

Mathematically, a wave function  $\Psi(x, t)$  representing a stationary state can be expressed as the product of a spatial part, which is independent of time, and a time-dependent phase factor. This relationship is depicted as follows:

$$\Psi(x, t) = \psi(x) \cdot e^{-iEt/\hbar}, \quad (1)$$

where  $\psi(x)$  is the time-independent spatial part of the wave function,  $E$  represents the energy of the state, and  $\hbar$  is the reduced Planck constant.

It's important to note that while the wave function in a stationary state undergoes a change in its overall complex phase due to the factor  $e^{-iEt/\hbar}$ , this phase evolution does not impact the probability density associated with the state. The constancy of the probability density is a defining characteristic of stationary states and is demonstrated as follows:

The probability density is the square of the absolute value of the wave function:

$$\rho(x, t) = \Psi^*(x, t)\Psi(x, t) = (\psi^*(x) \cdot e^{iEt/\hbar}) (\psi(x) \cdot e^{-iEt/\hbar}) \quad (2)$$

where  $\psi^*(x)$  is the complex conjugate of  $\psi(x)$ .

The phase factors  $e^{iEt/\hbar}$  and  $e^{-iEt/\hbar}$ , being complex conjugates, cancel each other out upon multiplication. This leads to the simplified expression:

$$\rho(x, t) = \psi^*(x) \cdot \psi(x) = |\psi(x)|^2, \quad (3)$$

which clearly shows that the probability density  $\rho(x, t)$  is independent of time. Thus, the 'stationary' nature of these states is manifested in the time-invariance of their probability densities.

## 2.1 Implications of Stationary States

- **Probability Density and Measurement** The probability density for a particle in a stationary state, given by  $|\psi(x)|^2$ , is time-independent. This characteristic ensures that the expectation values of all measurable quantities, such as position, momentum, and energy, remain constant over time. For a stationary state  $\psi(x)$ , the expectation value of an operator  $\hat{O}$  is given by:

$$\langle O \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{O} \psi(x) dx. \quad (4)$$

Since  $\psi(x)$  is independent of time, so is  $\langle O \rangle$ .

- **Quantum Superposition and Eigenstates** Stationary states, as eigenstates of the Hamiltonian, are fundamental to quantum mechanics, representing discrete energy levels and forming a complete set of states. Any general quantum state  $\Phi$  can be expressed as a superposition of these eigenstates:

$$\Phi(x, t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}, \quad (5)$$

where  $c_n$  are coefficients,  $\psi_n(x)$  are the eigenstates, and  $E_n$  are the corresponding energy levels.

### 3 Motion of Particle with Zero Potential

#### 3.1 Derivation

The time-independent Schrödinger equation (T.I.S.E.) for a quantum system is a fundamental equation in quantum mechanics. It's crucial to understand that the TISE can only be solved when the potential  $V(x)$  is specified. Different forms of  $V(x)$  correspond to different physical situations and lead to diverse quantum behaviors.

For a particle with  $V(x) = 0$ , representing a free particle in a region without potential energy influence, the T.I.S.E. is given by:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x), \quad (6)$$

where  $\hbar$  is the reduced Planck constant,  $m$  is the mass of the particle,  $\psi(x)$  describes the particle's state,  $E$  is the energy of the particle, and  $x$  is the particle's position.

To simplify the Schrödinger equation, we define  $k^2$  as:

$$k^2 = \frac{2mE}{\hbar^2}. \quad (7)$$

This leads to:

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0, \quad (8)$$

a second-order linear differential equation akin to the equation of a harmonic oscillator. For this equation, we have two types of solutions:

#### 3.2 Standing Wave Solutions

The standing wave solution is given by:

$$\psi_{\text{standing}}(x) = A \cos(kx) + B \sin(kx), \quad (9)$$

similar to solutions in an Infinite Square Well (more in the next pages). Standing wave solutions are typically explored in the context of specific boundary conditions, leading to quantization of energy levels.

#### 3.3 Traveling Wave Solutions

The traveling wave solution is represented as:

$$\psi_{\text{traveling}}(x) = Ce^{ikx} + De^{-ikx}, \quad (10)$$

reminiscent of a free particle. These solutions represent particles in motion, with the wave number  $k$  related to the particle's momentum. However, such plane wave solutions are not normalizable over an infinite domain, suggesting the use of wave packets to describe realistic free particle states.

## 4 Infinite Square Well

In quantum mechanics, the Infinite Square Well (ISW) is a model that describes a particle confined in a one-dimensional box with infinitely high potential barriers at both ends. The mathematical representation of the potential  $V(x)$  is defined as:

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq L, \\ \infty & \text{otherwise.} \end{cases} \quad (11)$$

where  $L$  represents the length of the well.

### 4.1 Infinite Square Well Eigenfunctions

The derivation of the energy eigenfunctions from the standing wave solutions in the context of an Infinite Square Well (ISW) involves several key steps.

#### Starting with Standing Wave Solutions

The general form of a standing wave solution in the ISW is:

$$\psi(x) = A \cos(kx) + B \sin(kx). \quad (12)$$

#### Applying Boundary Conditions

The wavefunction must be zero at both ends of the well. Specifically:

$$\text{At } x = 0 : \quad \psi(0) = A \cos(0) + B \sin(0) = A = 0, \quad (13)$$

$$\text{At } x = L : \quad \psi(L) = B \sin(kL) = 0. \quad (14)$$

#### Quantization of $k$

For non-trivial solutions ( $B \neq 0$ ), the condition  $\sin(kL) = 0$  must be met, leading to:

$$k = \frac{n\pi}{L}, \quad \text{where } n \text{ is a positive integer.} \quad (15)$$

#### Form of the Wavefunction

With  $A = 0$  and the quantized value of  $k$ , the wavefunction becomes:

$$\psi_n(x) = B \sin\left(\frac{n\pi x}{L}\right). \quad (16)$$

#### Normalization

The wavefunction is normalized to ensure the total probability of finding the particle in the well is 1:

$$\int_0^L |\psi_n(x)|^2 dx = 1. \quad (17)$$

Solving this integral, we find

$$B = \sqrt{\frac{2}{L}}$$

## Energy Eigenfunctions

Substituting the normalization constant  $B$  into the wavefunction, we obtain the normalized energy eigenfunctions for the ISW:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \quad (18)$$

**Remark:** This derivation is tailored to scenarios where the potential energy is primarily localized to the right side of the Energy axis. In cases where the system is centered precisely on the Energy axis, the overall procedure remains consistent. However, it's crucial to note that the specific boundary conditions will vary, leading to distinct quantum states in such scenarios.

## 4.2 Characteristics of ISW

- **Alternating Symmetry and Node Count Increment** The solutions of the ISW exhibit alternating symmetry with respect to the center  $x = \frac{L}{2}$ . Specifically, for odd  $n$ ,  $\psi_n(x)$  is symmetric, and for even  $n$ , it is antisymmetric. This symmetry property is evident from the sine function in the wave solutions:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \quad (19)$$

A symmetric wave function mirrors itself across the center, while an antisymmetric wave function takes on opposite values, hence the negative sign in the antisymmetric condition.

Additionally, each successive wave function  $\psi_{n+1}$  has one more node than  $\psi_n$ , where a node is a point where the wave function is zero.

- **Orthogonality of Solutions** The solutions are mutually orthogonal, meaning that the integral of the product of two different eigenfunctions,  $\psi_n(x)$  and  $\psi_m(x)$ , over the domain  $[0, L]$  equals  $\delta_{mn}$ .

$$\int_0^L \psi_n(x) \psi_m(x) dx = \delta_{mn} = \begin{cases} 0 & \text{if } m \neq n, \\ 1 & \text{if } m = n. \end{cases} \quad (20)$$

This orthogonality arises from the sinusoidal nature of the solutions and their alignment within the well.

- **Completeness of the Solution Set** The solutions form a complete set, allowing any square-integrable function  $f(x)$  defined on  $[0, L]$  to be expressed as a sum of these eigenfunctions:

$$\psi_{gen}(x) = \sum_{n=1}^{\infty} c_n \psi_n(x), \quad (21)$$

where  $c_n$  are the expansion coefficients. This property, known as completeness, is fundamental for expanding arbitrary states in terms of the eigenstates of the Hamiltonian.



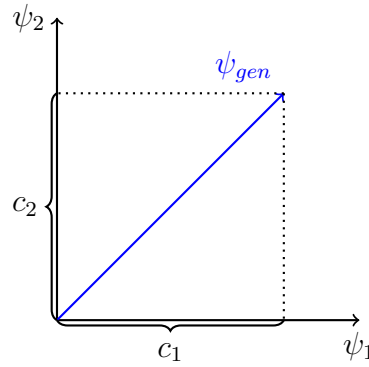


Figure 1: Conceptual visualization of the vector  $\psi_{gen}$  projected onto the basis vectors  $\psi_1$  and  $\psi_2$ .

Here we can clearly see:

$$\psi_{gen}(x) = c_1\psi_1(x) + c_2\psi_2(x)$$

**Remark:** It is imperative to acknowledge that the presented two-dimensional diagram simplifies a more complex reality. In actuality, the scenario entails an infinite-dimensional vector space, characterized by an unbounded series of mutually orthogonal basis functions, symbolically represented as  $\psi_n$ . Additionally, the components  $c_n$  involved are not restricted to real numbers but can extend to complex numbers. Despite these complexities, the two-dimensional representation provides a fundamental and accessible way to conceptualize the projections and components within the quantum mechanical framework.

### 4.3 Example

Consider a particle in an infinite square well of width  $L$ . The first three normalized wave functions and their corresponding energy levels are:

- For  $n = 1$ :

$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right), \quad E_1 = \frac{\pi^2 \hbar^2}{2mL^2}. \quad (22)$$

- For  $n = 2$ :

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right), \quad E_2 = \frac{4\pi^2 \hbar^2}{2mL^2}. \quad (23)$$

- For  $n = 3$ :

$$\psi_3(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right), \quad E_3 = \frac{9\pi^2 \hbar^2}{2mL^2}. \quad (24)$$

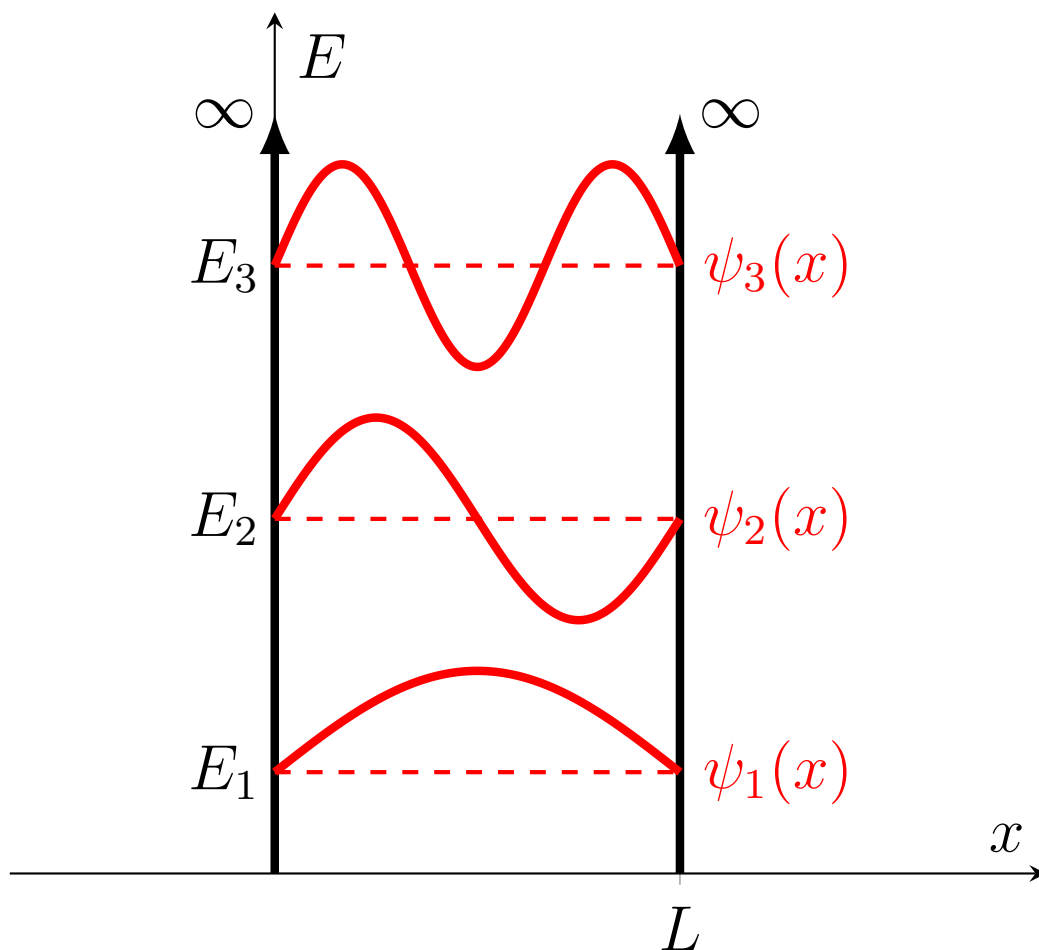


Figure 2: Solutions of the Infinite Square Well for  $n = 1, 2, 3$ .

## 5 The Free Particle

A free particle in quantum mechanics is an idealized concept representing a particle that is not subject to any external forces or potential influences. This contrasts with particles in bounded states, where external potentials or forces influence their behavior. This model is crucial for understanding the fundamental behavior of particles in a context devoid of external interactions, offering insights into intrinsic quantum properties.

### 5.1 Free Particle Eigenfunction

#### Starting with Traveling Wave Solutions

The general solution for a free particle in quantum mechanics is represented by a traveling wave solution. This is expressed as:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad (25)$$

where  $A$  and  $B$  are constants. The specific values of these constants are typically determined by the initial conditions or the boundary conditions of the problem which we do not have for this.

#### Simplification to a Single Traveling Wave

In some scenarios, particularly when considering unbounded space or specific initial conditions, it is appropriate to consider a single traveling wave. In such cases, the wave function simplifies to:

$$\psi(x) = Ce^{ikx}, \quad (26)$$

where  $C$  is a constant and  $k$  is the wave number. The wave number  $k$  is determined by the relation:

$$k = \pm \sqrt{\frac{2mE}{\hbar^2}}.$$

The positive and negative signs of  $k$  correspond to the wave traveling in the positive and negative  $x$ -directions, respectively.

#### Incorporating Time Dependence

To include the time-dependent aspect of the wave function, the full solution for a free particle is:

$$\Psi_k(x, t) = A \cdot \exp \left[ i \left( kx - \frac{\hbar k^2}{2m} t \right) \right], \quad (27)$$

This form of the wave function indicates a particle with constant momentum and energy, characteristic of a free particle. The exponential term involving time  $t$  represents the temporal evolution of the wave function.

## 5.2 Limitations of the Plane Wave Solution:

The plane wave solution for a free particle, represented by  $\Psi_k(x, t)$ , is not normalizable. This mathematical characteristic implies that such a solution cannot correspond to a physical state with a definite probability distribution. In quantum mechanics, this translates to the non-existence of a free particle with a precisely defined energy. The root of this issue lies in the continuous nature of  $k$  and the corresponding continuous energy spectrum for each  $k$  value. As a result, a single plane wave does not suffice to describe a realistic free particle in quantum mechanics.

## 5.3 Wave Packets and Continuous Spectrum

To address the non-normalizability and indefinite energy of plane waves,  $\Psi_{gen}$  for a free particle is expressed as a continuous superposition of  $\Psi_k$ , forming a wave packet:

$$\Psi_{gen}(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) \exp \left[ i \left( kx - \frac{\hbar k^2}{2m} t \right) \right] dk,$$

$$\text{with } g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, 0) e^{-ikx} dx \quad (\text{Shape Function}).$$

This formulation enables the creation of a normalizable wave function that realistically depicts a free particle.

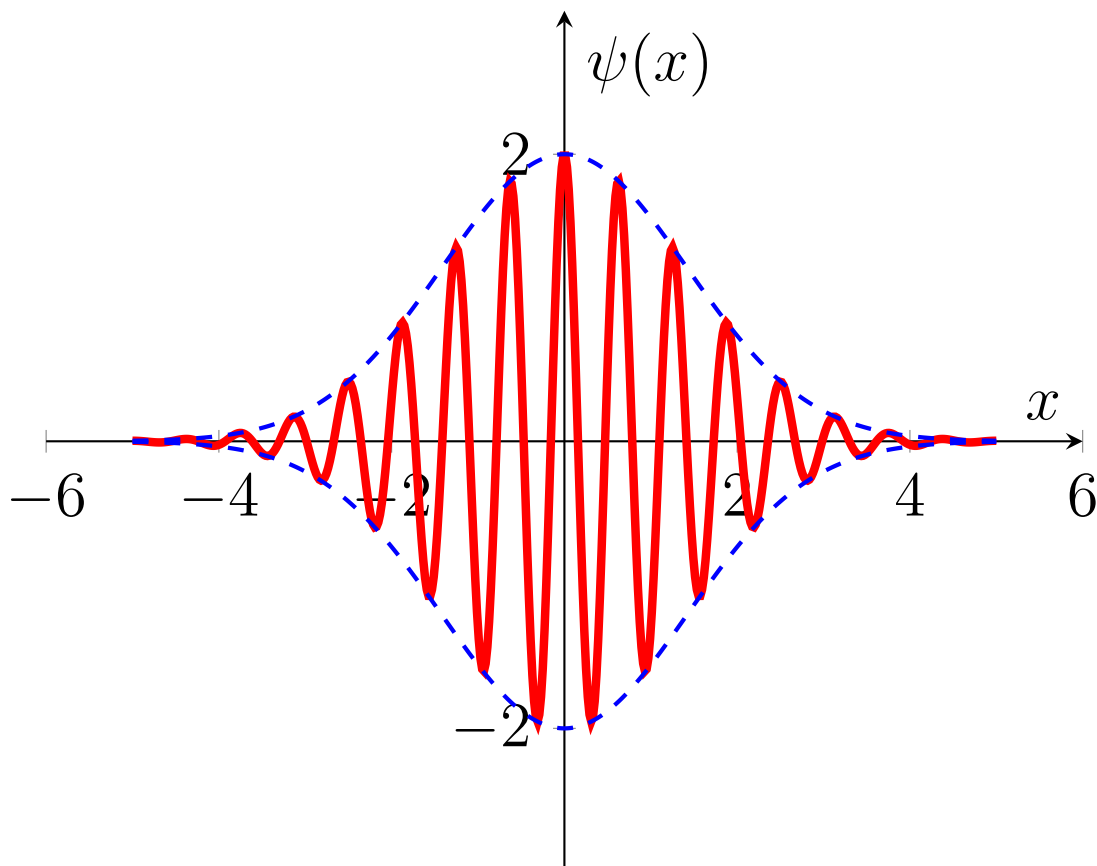


Figure 3: Wave packet formed by the superposition of multiple plane waves.

## 6 Commutators in Quantum Mechanics

Commutators are fundamental in quantum mechanics, providing insight into the properties of operators and their corresponding observables.

### 6.1 Definition of a Commutator

The commutator of two operators  $\hat{A}$  and  $\hat{B}$  is defined as:

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

It measures the non-commutativity of the operators, with  $[\hat{A}, \hat{B}] = 0$  indicating that  $\hat{A}$  and  $\hat{B}$  commute.

### 6.2 Commutator Properties and Identities

Commutators follow certain algebraic properties and identities:

- The commutator is anti-commutative:  $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$ .
- Addition identity:  $[\hat{A} + \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}]$ .
- Distributive property:  $[\hat{A}, \hat{B} \cdot \hat{C}] = [\hat{A}, \hat{B}] \hat{C} + \hat{B} [\hat{A}, \hat{C}]$ .

### 6.3 Common Commutators in Quantum Mechanics

Several commutators are particularly notable in quantum mechanics:

- Position and momentum:  $[\hat{x}, \hat{p}] = i\hbar$ .
- Position and a function of position:  $[\hat{x}, f(\hat{x})] = 0$ .
- Momentum and a function of momentum:  $[\hat{p}, f(\hat{p})] = 0$ .
- Hamiltonian and position:  $[\hat{H}, \hat{x}] = -\frac{\hbar^2}{m} \frac{\partial}{\partial x} = \frac{\hbar}{im} \hat{p}$ .

In the upcoming weeks, we will delve further into the topic of commutators, as they play a pivotal role in defining essential properties for measurements in quantum mechanics.