Fundamentals of Quantum Mechanics

Postulates, Wave Functions, Operators, Observables, and Matrix Representation

Daniele Toffoli

Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste

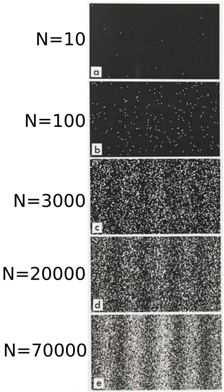
September 25, 2024

Outline

Outline

The Wave Function

Interpretation of the Double-Slit Experiment



Tonomura *et al.* (1989) Electron double-slit experiment

- A single electron passes through either one of the slits, A or B.
- The accumulated pattern looks like wave interference → superposition
- The term *wave function* is assigned to the probability amplitude with

$$P(x, y, z, t) \propto |\Psi(x, y, z, t)|^2$$

  where P is the probability of finding the particle at a position (x, y, z) at time t.
- $\Psi(x, y, z, t)$ is the so-called wave function.
- Note that $\Psi(x, y, z, t)$ can also be complex.

Outline

The Free Particle

The Wave Function of the Simplest System

Definition

A *free particle* is a point particle, which is under no potential. Within the wave-particle duality, it can be seen as a de Broglie wave with a definite wave length extending over the entire space.

- The momentum of such a particle for a given wavenumber $k = 2\pi/\lambda$ is $p = \hbar k$ or in 3D $\vec{k} = \hbar\vec{k}$.
- Its energy is $E = h\nu = \hbar\omega$.
- To this particle, we assign a wave function

$$\psi_p(x,t) = Ae^{i(kx-\omega t)}$$

- This function represents a delocalized state, meaning the probability of finding the particle is equally distributed across all positions.
- The momentum is well-defined, but the position is completely uncertain (delocalized over all space).

The Free Particle

The Momentum Operator

- Let us try to a mathematical operator (inspired by the classical wave equation) to access the momentum from the wave function
- These mathematical constructs will be called the momentum and energy *operators*

$$\hat{p} = -i\hbar \frac{d}{dx} \qquad \Rightarrow \qquad \hat{p}\psi_p(x,t) = \hbar k \psi_p(x,t) = p\psi_p(x,t)$$

- The three-dimensional equivalent is

$$\hat{\mathbf{p}} = -i\hbar\nabla$$

where ∇ is the gradient operator in Cartesian coordinates.

- The components of the momentum operator are:

$$\hat{\mathbf{p}} = \left(-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z}\right)$$

The Free Particle

Fourier Transform: Superposition of Momentum States

- A general wavefunction $\psi(x)$ can be written as a superposition of momentum eigenstates:

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \tilde{\psi}(p) e^{ipx/\hbar} dp$$

  where $\tilde{\psi}(p)$ is the wavefunction in the momentum representation.
- The function $\tilde{\psi}(p)$ is the Fourier transform of $\psi(x)$:

$$\tilde{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x) e^{-ipx/\hbar} dx$$

- This allows us to decompose any wavefunction into momentum eigenstates, linking the position and momentum representations.

Outline

Postulates of Quantum Mechanics

First Postulate: The State of a System

Postulate

At each instant, the state of a physical system is represented by a wave function $\Psi(\vec{r}, t)$.

- If the wave function is to be interpreted as a probability amplitude, it must be true that:

$$\int |\Psi(\vec{r}, t)|^2 d\vec{r} = 1$$

  This rule is called the *normalization* of the wave function.

- The quantity

$$P(\vec{r}, t) = |\Psi(\vec{r}, t)|^2$$

  is interpreted to be the probability of the particle to be at position $\vec{r}$ at time t.

Postulates of Quantum Mechanics

Aside: The Dirac Bracket Notation

- Since we use a lot of integration in quantum mechanics, a convenient shortcut is often used.
- In this notation, the scalar product of two wave functions $\Psi_1(\vec{r})$ and $\Psi_2(vr)$ (drop time dependence for brevity) is denoted as

$$\langle\Psi_1|\Psi_2\rangle \equiv \int \Psi_1^*(\vec{r})\Psi_2(\vec{r})d\vec{r}$$

- The two halves of the notation are called, respectively, the *bra*, and the *ket*

$$\langle\Psi_1| \rightarrow \text{bra}$$
$$|\Psi_2\rangle \rightarrow \text{ket}$$

- The bra and ket of a wave function are complex conjugates of one another

$$\langle\Psi_1|\Psi_2\rangle = \langle\Psi_2|\Psi_1\rangle^*$$

Postulates of Quantum Mechanics

Aside: The Dirac Bracket Notation

- Other properties:

$$\langle c\Psi_1|\Psi_2\rangle = c^*\langle\Psi_1|\Psi_2\rangle$$
$$\langle\Psi|\Psi\rangle = 1$$

- Two wave functions are said to be *orthogonal* if

$$\langle\Psi_1|\Psi_2\rangle = 0$$

- The bra and ket can be used to represent wave functions in the space, momentum and any other representation. This is why they are usually refered to as abstract *states* of the system.

Postulates of Quantum Mechanics

Second Postulate: The Superposition Principle

The Postulate

The states of a quantum system are linearly superposable.

- The space of states is a vector space, allowing superposition:

$$|\psi\rangle = a_1|\psi_1\rangle + a_2|\psi_2\rangle$$

where a_1 and a_2 are complex numbers.

Postulates of Quantum Mechanics

Third Postulate: Observables and Operators

Postulate

With every measurable quantity (observable) of the system, there is associated a *linear operator*.

- An operator $\hat{A}$ acts on a ket $|\psi\rangle$ as:

$$\hat{A}|\psi\rangle \rightarrow |\psi'\rangle = \hat{A}|\psi\rangle$$

- An operator is linear if

$$\hat{A}|c_1\Psi_1 + c_2\Psi_2\rangle = c_1\hat{A}|\Psi_1\rangle + c_2\hat{A}|\Psi_2\rangle$$

- The *eigenstate* $|\psi_a\rangle$ of an operator $\hat{A}$ is defined such that:

$$\hat{A}|\psi_a\rangle = a|\psi_a\rangle$$

  where a is an *eigenvalue*.

Postulates of Quantum Mechanics

Third Postulate: Observables and Operators

- For example, the momentum operator $\hat{p}$ in the position representation is given by:

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

and the position operator $\hat{x}$ is simply:

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

Postulates of Quantum Mechanics

Fourth Postulate: Measurement and Eigenvalues

Postulate

The only possible result of a measurement of an observable A is one of the eigenvalues of the corresponding operator $\hat{A}$.

- The totality of the eigenvalues of an operator $\hat{A}$ is called the *spectrum of* $\hat{A}$: $\hat{A}|\psi_n\rangle = a_n|\psi_n\rangle$.
- Since the results of measurements are real numbers, the spectrum must also be real.

$$\begin{aligned} \langle\psi_n|\hat{A}\psi_n\rangle &= a_n\langle\psi_n|\psi_n\rangle \\ \langle\hat{A}\psi_n|\psi_n\rangle &= a_n^*\langle\psi_n|\psi_n\rangle \end{aligned}$$

- Since a_n must equal a_n^*, $\hat{A}$ must satisfy $\langle\hat{A}\psi_n|\psi_n\rangle = \langle\psi_n|\hat{A}\psi_n\rangle$

Such operators are called *Hermitian.*

Postulates of Quantum Mechanics

Fourth Postulate: Measurement and Eigenvalues

- The Hermitian conjugate of an operator is defined via

$$\langle \phi | \hat{A}^\dagger | \psi \rangle = \langle \psi | \hat{A}^\dagger | \phi \rangle$$

- A Hermitian operator then satisfies

$$\hat{A}^\dagger = \hat{A}$$

  where $\hat{A}^\dagger$ is the Hermitian adjoint (or conjugate transpose) of $\hat{A}$.
- Example: The Hamiltonian operator $\hat{H}$ is Hermitian and represents the total energy of the system.

Postulates of Quantum Mechanics

Fourth Postulate: Measurement and Eigenvalues

- When measuring an observable, the system collapses to an eigenstate of the corresponding operator.
- If $\hat{A}$ is an operator with eigenfunctions ψ_n and eigenvalues a_n, then:

$$\hat{A}\psi_n = a_n\psi_n$$

- The probability of obtaining the measurement value a_n is given by:

$$P(a_n) = |\langle\psi_n|\Psi\rangle|^2$$

  where $\langle\psi_n|\Psi\rangle$ is the projection of the wavefunction Ψ onto the eigenfunction ψ_n.
- This concept is central to quantum mechanics, where each measurement yields one of the eigenvalues of the corresponding operator.

Postulates of Quantum Mechanics

Fifth Postulate: The expectation value of an operator

Postulate

If a series of measurements is made of the observable A on an ensemble of systems, described by the wave function Ψ, the *expectation* or average value is

$$\langle \hat{A} \rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

- The probability of obtaining an eigenvalue a_n when measuring an observable A is given by the square of the inner product of the state $|\psi\rangle$ with the eigenstate $|a_n\rangle$:

$$P(a_n) = |\langle a_n | \psi \rangle|^2$$

- After measurement, the system collapses into the eigenstate $|a_n\rangle$.

Postulates of Quantum Mechanics

Sixth Postulate: Time Evolution of a System

Postulate

The system evolves in time according to the time-dependent Schrödinger equation:

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$$

where $\hat{H}$ is the so-called *Hamiltonian* of the system.

- The Hamiltonian operator is given by

$$\hat{H} = \hat{T} + \hat{V}$$

  where $\hat{T} = \frac{\hbar^2}{2m}\nabla^2$ is the kinetic energy operator and $\hat{V}$ is the potential energy operator.
- The eigenvalues of the Hamiltonian operator are the energy spectrum of the system:

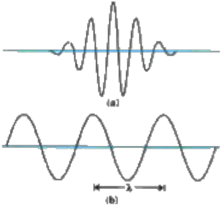
$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

Outline

Heisenberg Uncertainty Principle and Commutators

Motivation

- Classical physics suggests that we can measure the position and momentum of any object with unlimited precision.
- In quantum mechanics, once, say, the momentum is measured, the wave function collapses to a momentum eigenstate and the particle then has equal probability of being at any point in space



- This means that momentum and position cannot be measured simultaneously.

Heisenberg Uncertainty Principle and Commutators

The Uncertainty Principle

- The Heisenberg Uncertainty Principle states that certain pairs of physical quantities, such as position and momentum, cannot both be precisely measured at the same time.
- For two operators $\hat{A}$ and $\hat{B}$, this principle is expressed as:

$$(\Delta A)^2(\Delta B)^2 \geq -\frac{1}{4}(\langle [A, B] \rangle)^2$$

  where ΔA is the uncertainty in observable A and ΔB is the uncertainty observable B.
- This inequality defines a fundamental limit to the precision of measurements in quantum mechanics.
- This can be understood from the wave nature of particles: a wave localized in space has a wide spread in momentum.
- It also means that the order in which the momentum and position is measured also matters $\rightarrow$ *non-commutativity*.

Heisenberg Uncertainty Principle and Commutators

Commutativity

The Commutator

For two operators $\hat{A}$ and $\hat{B}$, the *commutator* is defined as:
$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

- The commutator is also an operator itself.
- For position and momentum, we apply the commutator to a free particle in one-dimension

$$[\hat{x}, \hat{p}]Ce^{ikx} = Cx\left(-i\hbar\frac{d}{dx}\right)e^{ikx} - C\left(-i\hbar\frac{d}{dx}(xe^{ikx})\right) = i\hbar Ce^{ikx}.$$

- The commutator between $\hat{x}$ and $\hat{p}$ is then

$$[\hat{x}, \hat{p}] = i\hbar \longrightarrow \Delta x \Delta p \geq \frac{\hbar}{2}$$

- Those operators whose commutators are zero are said to *commute* and can be measured simultanously, e.g. $\hat{T}$ and $\hat{p}$

Outline

Matrix Representation

Expanding a Wavefunction in a Basis

- Consider a Hermitian operator with normalized eigenstates $\{\phi_n\}$ such that

$$\langle \phi_n | \phi_n \rangle = 1$$

- Now consider two separate eigentates with two unequal eigenvalues:

$$\hat{A}|\phi_n\rangle = a_n|\phi_n\rangle \qquad \text{and} \qquad \hat{A}|\phi_m\rangle = a_m|\phi_m\rangle$$

- Next, using the Hermiticity of $\hat{A}$, let us develop the expression

$$(a_n - a_m)\langle \phi_n | \phi_m \rangle = \langle \hat{A}\phi_n | \phi_m \rangle - \langle \phi_n | \hat{A}\phi_m \rangle = 0$$

- Since $a_n \neq a_m$, then it must be true that $\langle \phi_n | \phi_m \rangle = 0$.
- The two eigenstates are then said to be orthonormal:

$$\langle \phi_n | \phi_m \rangle = \delta_{nm} = \begin{cases} 0 & n \neq m \\ 1 & n = m \end{cases}$$

Matrix Representation

Expanding a Wavefunction in a Basis

- Using the basis introduced in the previous slide, let us write a general wave function as

$$\Psi(x) = \sum_n c_n \phi_n(x)$$

- Here, the coefficients c_n are the projection of $\Psi(x)$ onto the basis functions:

$$c_n = \langle \phi_n | \Psi \rangle = \int \phi_n^*(x) \Psi(x) dx$$

- The choice of basis depends on the problem at hand. Common bases include:
  - Energy eigenstates (for the Hamiltonian)
  - Position or momentum eigenstates
  - Harmonic oscillator states, etc.

Matrix Representation

Operators in a Basis Representation

- In the basis $\{\phi_n(x)\}$, operators can be represented by matrices.
- Consider an operator $\hat{A}$ acting on the wavefunction $\Psi(x)$. The action of $\hat{A}$ on a basis function is given by:

$$\hat{A}\phi_n(x) = \sum_m A_{mn}\phi_m(x)$$

where A_{mn} are the matrix elements of $\hat{A}$ in this basis:

$$A_{mn} = \langle \phi_m | \hat{A} | \phi_n \rangle$$

- The operator $\hat{A}$, therefore, becomes a matrix **A** with elements A_{mn} in this basis.
- The matrix representation simplifies the computation of observables, eigenvalues, and eigenstates.

Matrix Representation

Vector Representation of the Wavefunction

- Once a basis is chosen, the wavefunction $\Psi(x)$ is represented by a vector of expansion coefficients:

$$\Psi(x) = \sum_n c_n \phi_n(x) \quad \rightarrow \quad |\Psi\rangle = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$$

- Similarly, an operator $\hat{A}$ is represented by a matrix $\mathbf{A}$:

$$\hat{A}|\Psi\rangle = \mathbf{Ac}$$

- For example, applying $\hat{A}$ to $|\Psi\rangle$ results in a new wavefunction:

$$\mathbf{A} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} \sum_j A_{1j} c_j \\ \sum_j A_{2j} c_j \\ \vdots \end{pmatrix}$$