

Chapter 4 – Elements of the Wave Function Formalism. Schrödinger Equation. Infinite Potential Well

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Wave Function

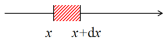
Wave Function

In quantum mechanics the state of a particle is represented by a **wave-function**. It is usually denoted by the Greek letter Ψ . The wave function is in general complex-valued. For the wave function in the position representation in 1D and in 3D, respectively,

$$\Psi = \Psi(x, t), \quad \Psi = \Psi(\vec{r}, t),$$

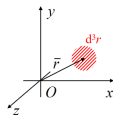
Interpretation (Born)

$$|\Psi(x, t)|^2 dx = \Psi^*(x, t) \Psi(x, t) dx$$



probability of finding the particle in
($x, x + dx$) at instant t

$$|\Psi(\vec{r}, t)|^2 d^3r = \Psi^*(\vec{r}, t) \Psi(\vec{r}, t) d^3r$$



probability of finding the particle in
the element of volume d^3r around \vec{r}
at instant t

Probabilistic Interpretation of Wave Function

Note. In the language of probability: x and \vec{r} are the values of a random variable, whereas $|\Psi(x, t)|^2$ and $|\Psi(\vec{r}, t)|^2$ are the corresponding probability density functions.

Consequently

$$\int_a^b |\Psi(x, t)|^2 dx$$

is the probability of finding the particle in an interval $[a, b]$, and

$$\iiint_A |\Psi(\vec{r}, t)|^2 d^3r$$

is the probability of finding the particle in a solid region A .

Normalization

Functions satisfying the condition

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1 \quad \text{or} \quad \iiint_{\mathbb{R}^3} |\Psi(\vec{r}, t)|^2 d^3r = 1$$

are said to be **normalized**.

- If $\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx < \infty$ or $\iiint_{\mathbb{R}^3} |\Psi(\vec{r}, t)|^2 d^3r < \infty$, then Ψ is said to be **square-integrable**.
- Square-integrable functions (with the usual operations of function addition and multiplication by a scalar) form a linear space denoted as $\mathcal{L}^2(\mathbb{R})$ or $\mathcal{L}^2(\mathbb{R}^3)$.

Trajectory, Average Position, and Uncertainty of Position

Implication. Quantum mechanics gives up on the idea of trajectory in the classical sense.



determinism



probability

Hence, we will rather use the **average position** of the particle in the state represented by the function Ψ (furthermore we will give the formulas in the 1D-version)

$$\langle x \rangle_{\Psi} = \int_{-\infty}^{\infty} x |\Psi(x, t)|^2 dx = \int_{-\infty}^{\infty} \Psi^*(x, t) x \Psi(x, t) dx.$$

Consequently, the **variance of the position** is given by

$$\begin{aligned} (\Delta_x^{(\Psi)})^2 &= \langle (x - \langle x \rangle_{\Psi})^2 \rangle_{\Psi} = \langle x^2 - 2x\langle x \rangle_{\Psi} + \langle x \rangle_{\Psi}^2 \rangle_{\Psi} \\ &= \langle x^2 \rangle_{\Psi} - 2\langle x \rangle_{\Psi} \langle x \rangle_{\Psi} + \langle x \rangle_{\Psi}^2 = \langle x^2 \rangle_{\Psi} - \langle x \rangle_{\Psi}^2 \end{aligned}$$

The **standard deviation** (a.k.a. **dispersion** or **uncertainty**) of the position is $\Delta_x^{(\Psi)} = \sqrt{\langle x^2 \rangle_{\Psi} - \langle x \rangle_{\Psi}^2}$.

Stationary States

If $|\Psi(x,t)|^2 = \Phi(x)$, i.e. the modulus square does not depend on time, then the state represented by Ψ is called a stationary state.

Observation. For a stationary state, $\langle x \rangle_\Psi$ and $\Delta_x^{(\Psi)}$ are time-independent.

Example. The wave function $\Psi(x, t) = e^{-\frac{i}{\hbar}Et}f(x)$, where E is a constant and f is a square-integrable function, is representing a quantum system (particle) in a stationary state.

Mathematical Appendix (I). Inner Product

Inner Product

In the space $\mathcal{L}^2(\mathbb{R})$ the **inner product** $\langle \cdot, \cdot \rangle$ (an equivalent of the scalar product in the space of usual vectors) can be introduced as

$$\langle \Psi, \Phi \rangle \stackrel{\text{def}}{=} \int_{-\infty}^{\infty} \underbrace{\Psi^*(x, t)}_{\text{red underline}} \Phi(x, t) dx, \quad \text{💬}$$

where $\Psi^*(x, t)\Phi(x, t)$ is in general a complex number.

Observation (exercise). For any Ψ, Φ_1 and $\Phi_2 \in \mathcal{L}^2(\mathbb{R})$ and $\alpha \in \mathbb{C}$:

$$\langle \Psi, \Phi_1 + \Phi_2 \rangle = \langle \Psi, \Phi_1 \rangle + \langle \Psi, \Phi_2 \rangle \quad (1)$$

$$\langle \Psi, \alpha \Phi \rangle = \alpha \langle \Psi, \Phi \rangle \quad (2)$$

$$\underbrace{\langle \Psi, \Phi \rangle}_{\text{red underline}} = \langle \Phi, \Psi \rangle^* \quad (3)$$

$$\langle \Psi, \Psi \rangle \geq 0; \quad \langle \Psi, \Psi \rangle = 0 \Leftrightarrow \Psi \equiv 0 \quad (4)$$

*Comment**. Any functional satisfying the four axioms (1)–(4) is an inner product.

The formula $\langle \Psi, \Phi \rangle$ quoted above is just a particular realization of the inner product in $\mathcal{L}^2(\mathbb{R})$.

Note

- (3) and (2) imply $\langle \alpha \Psi, \Phi \rangle = \alpha^* \langle \Psi, \Phi \rangle$.
 - * (4) induces the norm $\|\Psi\| = \sqrt{\langle \Psi, \Psi \rangle}$ (and hence the metric $d(\Psi, \Phi) = \|\Psi - \Phi\|$).
 - ** A linear space with an inner product is called a *unitary space* and a unitary space that is complete in the norm-introduced metric is called a *Hilbert space*.
 - *** Any Hilbert space is a Banach space, but a Banach space is not necessarily a Hilbert space.
-

Examples. Rewrite using the inner product notation.

(a) Average position $\langle x \rangle_\Psi$, where x is a real number.

$$\int_{-\infty}^{\infty} \Psi^*(x, t) x \Psi(x, t) dx = \langle \Psi, x \Psi \rangle$$

(b) The normalization condition.

$$\langle \Psi, \Psi \rangle = 1$$

Physical Quantities

Physical Quantities and Hermitian Operators

In quantum mechanics, physical (i.e. measurable) quantities are represented by **Hermitian operators**.

What is an operator?

An operator transforms one function into another: $\hat{A}\Psi = \Phi$. We will use hats $\hat{}$ to denote operators.

Examples.

$$\frac{\partial}{\partial x}(x^4) = 4x^3$$

differentiation

$$\hat{\alpha}f(x) = \alpha \cdot f(x)$$

multiplication by a scalar

$$\hat{Q}f(x) = (f(x))^*$$

complex conjugation

Hermitian Operators

If $\langle \hat{B}\Psi, \Phi \rangle = \langle \Psi, \hat{A}\Phi \rangle$ for all $\Psi, \Phi \in \mathcal{L}^2(\mathbb{R})$, then \hat{B} is called the **Hermitian conjugate** of \hat{A} and it is denoted as \hat{A}^\dagger . (that is $\langle \hat{A}^\dagger \Psi, \Phi \rangle = \langle \Psi, \hat{A}\Phi \rangle$)

Operator \hat{A} is said to be **Hermitian**, if $\hat{A}^\dagger = \hat{A}$ (that is $\langle \hat{A}\Psi, \Phi \rangle = \langle \Psi, \hat{A}\Phi \rangle$ for all Ψ and Φ .)

Examples. Which of the given operators are Hermitian?

(a) the position operator (in the position representation) $\hat{x} = x$, which is just the multiplication by a (real) number x .

Check whether $\hat{x} = \hat{x}^\dagger$.

$$\begin{aligned}\langle \Psi, \hat{x}\Phi \rangle &= \int_{-\infty}^{\infty} \Psi^* \hat{x}\Phi \, dx = \int_{-\infty}^{\infty} \Psi^* (x \cdot \Phi) \, dx \stackrel{x=x^*}{=} \int_{-\infty}^{\infty} (x \cdot \Psi)^* \Phi \, dx \\ &= \int_{-\infty}^{\infty} (\hat{x}\Psi)^* \Phi \, dx = \langle \hat{x}\Psi, \Phi \rangle\end{aligned}$$

Therefore \hat{x} is Hermitian.

(b) the momentum operator (in the position representation)

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

where i is the imaginary unit ($i^2 = -1$).

* The form of the momentum operator can be derived by studying infinitesimal translations (c.f. Noether's theorem).

Check whether $\hat{p}^\dagger = \hat{p}$ (i.e. whether \hat{p} is Hermitian).

$$\begin{aligned}\langle \Psi, \hat{p}\Phi \rangle &= \int_{-\infty}^{\infty} \Psi^* \hat{p}\Phi \, dx = \int_{-\infty}^{\infty} \Psi^* \left(-i\hbar \frac{\partial}{\partial x} \Phi\right) dx \quad \text{💬} \\ &\stackrel{\text{by parts}}{=} [-i\hbar \Psi^* \Phi]_{-\infty}^{+\infty} + \int_{-\infty}^{\infty} (i\hbar \frac{\partial}{\partial x} \Psi^*) \Phi \, dx \\ &= \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial}{\partial x} \Psi\right)^* \Phi \, dx = \int_{-\infty}^{\infty} (\hat{p}\Psi)^* \Phi \, dx = \langle \hat{p}\Psi, \Phi \rangle\end{aligned}$$

Therefore \hat{p} is Hermitian.

Average Value

The **average value** of a physical quantity A in state Ψ is

$$\langle A \rangle_{\Psi} = \langle \Psi, \hat{A} \Psi \rangle$$

where \hat{A} is the corresponding (Hermitian) operator.

Note

- $\langle A \rangle_{\Psi}$ is always real (simple exercise: use Hermiticity & properties of the inner product).
- Consequently, the standard deviation $\Delta_A^{(\Psi)} = \sqrt{\langle A^2 \rangle_{\Psi} - (\langle A \rangle_{\Psi})^2}$.
- $\Delta_x^{(\Psi)} \Delta_p^{(\Psi)} \geq \hbar/2$ is known as **Heisenberg Uncertainty Principle** and will be derived later.

Other Important Operators. The Hamiltonian

(a) kinetic energy operator

$$\hat{K} = \frac{\hat{p}^2}{2m} = \frac{(-i\hbar \frac{\partial}{\partial x})^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

(b) potential energy operator (multiplication by scalar $V(x)$)

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

(c) total energy operator — the **Hamiltonian**

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

Exercise. Argue that they are Hermitian.

(Hint. Use the Hermiticity of \hat{p} and \hat{x} .)

Schrödinger Equation

| | classical mechanics | quantum mechanics |
|--------------------------------|---|--------------------------------------|
| particle's state | position $\vec{r} = \vec{r}(t)$ | wave function $\Psi = \Psi(x, t)$ |
| time-evolution of the state | Newton's equation of motion $\vec{F} = d\vec{p}/dt$ | ? |

What should stand at the position of the question mark is the **Schrödinger equation**. The Schrödinger equation is the quantum-mechanical equation of motion determining the time-evolution of particle's state.

Schrödinger Equation. Motivation (not 'Derivation')

Recall the wave equation of photons (e-m wave)

$$\frac{\partial^2 \tilde{\xi}}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \tilde{\xi}}{\partial t^2}.$$

For a plane wave $\tilde{\xi} = \tilde{\xi}_0 e^{i(kx - \omega t)}$, we have $\begin{cases} \partial^2 \tilde{\xi} / \partial x^2 = -k^2 \tilde{\xi} \\ \partial^2 \tilde{\xi} / \partial t^2 = -\omega^2 \tilde{\xi} \end{cases}$. Hence

$$k^2 = \frac{\omega^2}{c^2} \rightarrow \omega = kc \quad \begin{matrix} p = \hbar k, E = \hbar \omega \\ \rightarrow \end{matrix} \quad \boxed{E = pc.}$$

For non-relativistic particles (e.g. electrons) in a potential force field, the corresponding relationship reads $\boxed{E = \frac{p^2}{2m} + V}$, where V is the potential energy. Using de Broglie relations $E = \hbar\omega$ and $p = \hbar k$, it can be rewritten as

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + V.$$

For a plane wave, the operators that yield the first term on the lhs and the first term on the rhs are $\hbar\omega \sim i\hbar \frac{\partial}{\partial t}$ and $\frac{\hbar^2 k^2}{2m} \sim -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$.

1D Schrödinger Equation

The state of a particle with mass m , moving in a force field with the potential energy $V(x)$, is represented by the wave function $\Psi(x, t)$ which evolves with time according to the **Schrödinger equation**.

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

Terminology. In QM the term “potential” is commonly used instead of “potential energy”.

Comments

- 1 Schrödinger equation is a 2^{nd} order partial differential equation.
- 2 Schrödinger equation is also a linear equation, i.e. if Ψ_1, Ψ_2 are solutions to the same Schrödinger equation and α, β are any complex numbers, then $\alpha\Psi_1 + \beta\Psi_2$ is also a solution to that equation.

Digression. Superposition Principle

If Ψ_1 and Ψ_2 are wave functions describing two states of a particle, and α, β are any complex numbers, then $\alpha\Psi_1 + \beta\Psi_2$ is the wave function representing another possible state of that particle.

Note.* Postulating that states of a particle are elements (vectors) from a Hilbert space already implies the superposition principle (Hilbert space is a linear space).

Example. *Quantum Bit*

Recall that a classical bit can be either “not set” $\boxed{0}$ or “set” $\boxed{1}$. On the contrary, for any two-level system with states $\boxed{0}$ or $\boxed{1}$, the quantum bit (**qubit**) that can be defined on this system, may be in any of the superposition states $\alpha\boxed{0} + \beta\boxed{1}$.

Stationary (Time-Independent) Schrödinger Equation

1D Time-Dependent Schrödinger Equation

Recalling the form of the Hamiltonian, the time-dependent Schrödinger equation can also be rewritten in a more compact form

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

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

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

where \hat{H} is the Hamiltonian, which represents the total energy of the particle.

Separation of Variables

Suppose that \hat{H} does not depend on time explicitly. We will be looking for wavefunctions that are solutions to the Schrödinger equation in the form $\Psi(x, t) = f(t)\psi(x)$.

$$\hat{H}(f(t)\psi(x)) = i\hbar \frac{\partial}{\partial t}(f(t)\psi(x))$$

\Downarrow

$$f(t)[\hat{H}\psi(x)] = \psi(x)[i\hbar \frac{df(t)}{dt}]$$



\Downarrow

$$\frac{\hat{H}\psi(x)}{\psi(x)} = \frac{i\hbar \frac{df(t)}{dt}}{f(t)} = E$$

where E is the separation constant and each term has to be equal to this constant (proved by contraposition).

Hence, a single PDE turns into two ODEs:

1

$$\frac{\hat{H}\psi(x)}{\psi(x)} = E \quad \Rightarrow \quad \boxed{\hat{H}\psi(x) = E\psi(x)}$$

Note that here \hat{H} is an operator and E is a number, so it is an eigenproblem for the Hamiltonian. Its solution is a set of E — eigenvalues (eigenenergies or energy levels) and $\psi(x)$ — eigenfunctions corresponding to eigenvalues E .

2

$$i\hbar \frac{df(t)}{dt} = E \quad \Rightarrow \quad i\hbar \frac{df(t)}{dt} = Ef(t) \quad \Rightarrow \quad \boxed{f(t) = e^{-\frac{i}{\hbar}Et}}$$

where E is the eigenenergy.

Comment. The multiplicative constant resulting from solving the differential equation is included in ψ (eventually, we need to normalize the wavefunction anyway).

Stationary Schrödinger Equation

With the explicit form of \hat{H} , the eigenproblem for the Hamiltonian can be written as

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x).$$

This equation is known as the **time-independent Schrödinger equation** or the **stationary Schrödinger equation**.

The wave function ψ should satisfy the following requirements

- 1 ψ is continuous;
- 2 ψ' is continuous (may be relaxed for singular potentials);
- 3 ψ is square-integrable if it represents a bound state.

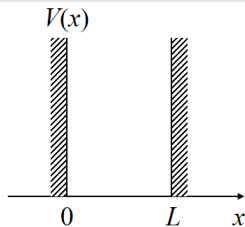
Full solution (with time dependence) corresponding to an eigenvalue E (remember to normalize!)

$$\Psi_E(x, t) = e^{-\frac{i}{\hbar}Et} \psi_E(x)$$

Example. Particle in Infinite Potential Well

Infinite Potential Well

$$V(x) = \begin{cases} 0, & \text{for } 0 < x < L \\ \infty, & \text{otherwise} \end{cases}$$



No particle can be found outside of $[0, L]$, i.e. $\psi(x) \equiv 0$ for $x < 0$ or $x > L$.

Inside of $[0, L]$, we have $V(x) \equiv 0$ and the stationary Schrödinger equation reads

$$\begin{cases} -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \\ \psi(0) = \psi(L) = 0 \quad (\text{continuity of } \psi) \end{cases}$$

Hence, formally, we need to solve a boundary value problem.

$E = ?$ $\psi_E(x) = ?$

Solution: Eigenvalues (Energy Levels)

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

where $k^2 \stackrel{\text{def}}{=} 2mE/\hbar$. Since $k^2 > 0$, the general **solution** to this ODE is

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

Eigenvalues

Apply the continuity conditions (boundary conditions):

$$(1) \quad \psi(0) = A = 0 \quad \Longrightarrow \quad \boxed{\psi(x) = B \sin kx}$$

$$(2) \quad \psi(L) = B \sin kL = 0 \quad \Longrightarrow \quad kL = n\pi \quad \Longrightarrow \quad k = \frac{n\pi}{L} = k_n$$

where $n = 1, 2, \dots$ is the quantum number. (**Why $n \neq 0$?**)

But $k^2 = \frac{2mE}{\hbar^2}$, hence

$$\boxed{E = E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2, \quad n = 1, 2, \dots}$$



Energy Levels in Infinite Potential Well. Discussion

discrete spectrum

eigenenergy E

$$E_3 = 9E_1$$

$$E_2 = 4E_1$$

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2}$$

0



Solution: Eigenfunctions

$$\psi(x) = \psi_n(x) = \begin{cases} B \sin k_n x, & \text{for } 0 \leq x \leq L \\ 0, & \text{otherwise} \end{cases}$$

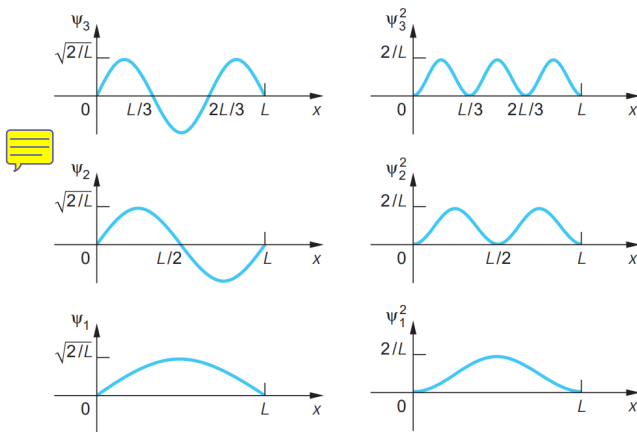
But $k_n = n\pi/L$, hence

$$\psi_n(x) = \begin{cases} B \sin \frac{n\pi}{L} x, & \text{for } 0 \leq x \leq L \\ 0, & \text{otherwise} \end{cases}$$

The normalization condition $\langle \psi_n, \psi_n \rangle = 1$ (that is, explicitly, $\int_{-\infty}^{\infty} \psi_n^*(x) \psi_n(x) dx = 1$) yields $B = \sqrt{2/L}$. Hence

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x, & \text{for } 0 \leq x \leq L \\ 0, & \text{otherwise} \end{cases}$$

Wave Functions in Infinite Potential Well. Discussion



Solutions to time-dependent equation (stationary states)

$$\psi_n(x, t) = e^{-\frac{i}{\hbar} E_n t} \psi_n(x) = \sqrt{\frac{2}{L}} e^{-\frac{\hbar^2 \pi^2}{2mL^2} n^2 t} \sin \frac{n\pi}{L} x$$

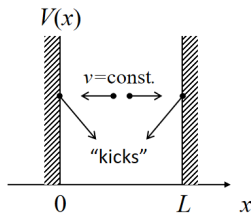
for $0 \leq x \leq L$ and zero otherwise.

The Correspondence Principle

Question: *How does the solution to the Schrödinger equation compare with classical mechanics?*

- Discrete spectrum vs continuous spectrum of energy levels.
- But in the limit of large n classical results expected (the correspondence principle).

Classical analysis



Probability of finding the particle in $(x, x + dx)$

$$\frac{dt}{T} = \frac{2 \frac{dx}{v}}{2 \frac{L}{v}} = \frac{1}{L} dx$$

The Correspondence Principle

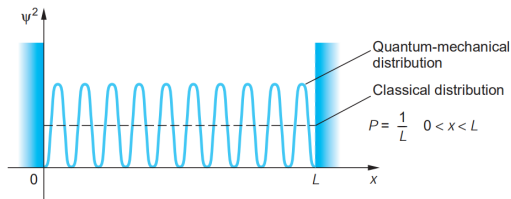
Hence, the classical probability density: $g_{cl}(x) = \frac{1}{L}$ for $0 \leq x \leq L$, and zero otherwise.

Quantum-mechanical probability density

$$g_q(x) = |\Psi_n(x, t)|^2 = |\psi_n(x)|^2 = \frac{2}{L} \sin^2 \left(\frac{n\pi}{L} x \right); \text{ for } 0 \leq x \leq L$$

For $n \rightarrow \infty$, $g_q(x)$ can be replaced by the average value


$$g_q(x) \xrightarrow{n \rightarrow \infty} \frac{1}{L} \int_0^L |\psi_n(x)|^2 dx = \frac{1}{L}$$



Schrödinger Equation with an Initial Condition

Initial Condition

Question: *How to incorporate an initial condition?*

$$\begin{cases} \hat{H}\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \\ \Psi(x, 0) = \Phi(x) \end{cases}$$


Idea

- 1 Solve the stationary Schrödinger equation $\hat{H}\psi_n(x) = E_n\psi_n(x)$, i.e. find eigenvalues and eigenfunctions of \hat{H} .
- 2 Express the solution to the time-dependent Schrödinger equation as $\Psi(x, t) = \sum_n c_n e^{\frac{i}{\hbar} E_n t} \psi_n(x)$, where c_n 's are to be found.
- 3 Find c_n 's by using the initial condition $\Psi(x, 0) = \sum_n c_n \psi_n(x)$.

For Steps 2 and 3, can we construct such expansions? In other words, do ψ_n 's form a basis of the corresponding space?

Mathematical Appendix (II).

Properties of Hermitian Operators

Let \hat{A} be the Hermitian operator corresponding to a physical quantity A . Then

- (1) Eigenvalues of \hat{A} are real.
- (2) Eigenfunctions corresponding to different eigenvalues are orthogonal (i.e. $\langle \psi_n, \psi_m \rangle = 0$ if $n \neq m$).
- (3) any square-integrable function can be represented as $\Psi = \sum_n c_n \psi_n$ where ψ_n 's are the eigenfunctions of \hat{A} .

Note. Statements (2) and (3) will get slightly modified if there are uncountably many eigenvalues of \hat{A} .

*** Statement (3) follows from the spectral theorem.

Justification of (1) and (2)

$$\left\{ \begin{array}{l} \hat{A}\psi_n = \alpha_n\psi_n \\ \hat{A}\psi_m = \alpha_m\psi_m \end{array} \right. \begin{array}{c} \langle \psi_m, \dots \rangle \\ \langle \dots, \psi_n \rangle \end{array} \Rightarrow \left\{ \begin{array}{l} \langle \psi_m, \hat{A}\psi_n \rangle = \alpha_n \langle \psi_m, \psi_n \rangle \\ \langle \hat{A}\psi_m, \psi_n \rangle = \alpha_m^* \langle \psi_m, \psi_n \rangle \end{array} \right.$$

Since \hat{A} is Hermitian

$$\left\{ \begin{array}{l} \langle \psi_m, \hat{A}\psi_n \rangle = \alpha_n \langle \psi_m, \psi_n \rangle \\ \langle \psi_m, \hat{A}\psi_n \rangle = \alpha_m^* \langle \psi_m, \psi_n \rangle \end{array} \right.$$

Subtracting both equations side by side

$$\boxed{0 = (\alpha_n - \alpha_m^*) \langle \psi_m, \psi_n \rangle}$$

- If $n = m$, then since $\langle \psi_n, \psi_n \rangle \neq 0$, we have $\alpha_n = \alpha_n^*$, i.e. α_n is real [property (1)].
- If $n \neq m$, and $\alpha_n \neq \alpha_m$, then $\langle \psi_n, \psi_m \rangle = 0$, i.e. ψ_n and ψ_m are orthogonal to each other [property (2)].

Incorporating an Initial Condition. Expansion in Eigenstates

$$\Psi(x, t) = \sum_n c_n e^{-\frac{i}{\hbar} E_n t} \psi_n(x)$$

Assume $\langle \psi_n, \psi_n \rangle = 1$ (normalized)

$$\Psi(x, 0) = \Phi(x) = \sum_n c_n \psi_n(x)$$

Find

$$\langle \psi_m, \Phi \rangle = \langle \psi_m, \sum_n c_n \psi_n \rangle = \sum_n c_n \langle \psi_m, \psi_n \rangle = \sum_n c_n \delta_{mn} = c_m$$

$$\boxed{c_m = \langle \psi_m, \Phi \rangle}$$

Hence, each of the coefficients c_n is the orthogonal projection of Φ onto ψ_n .

[Recall cartesian components of vectors in a 3D Euclidean space.]

Incorporating an Initial Condition

Hence, the time dependent solution satisfying the given initial condition

$$\Psi(x, t) = \sum_n \langle \psi_n, \Phi \rangle e^{-\frac{i}{\hbar} E_n t} \psi_n(x)$$

where $\langle \psi_n, \Phi \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) \Phi(x) dx$.

Exercises (Also, see problem set)

- (a) For a particle in an infinite potential well, find $\Psi(x, t)$ for $t > 0$, if $\Psi(x, 0) = \frac{1}{\sqrt{2}}(\psi_1(x) + \psi_2(x))$ (linear combination of only two eigenfunctions \Rightarrow only $c_1, c_2 \neq 0$).
- (b) For a particle in an infinite potential well, find $\Psi(x, t)$ for $t > 0$, if $\Psi(x, 0) = \sqrt{\frac{30}{L^5}}x(x - L)$ (infinitely many eigenfunctions contribute \Rightarrow infinitely many c_n 's $\neq 0$).
- (c) Expanding well (see the applet on the St. Andrews University's website).

Comment. Interpretation of the Expansion Coefficients

Example. Suppose that at some instant, a quantum system is described by the wavefunction

$$\psi = \sqrt{\frac{2}{5}}\psi_1 + \sqrt{\frac{3}{5}}\psi_3$$

where ψ_1 and ψ_3 are normalized eigenfunctions of the Hamiltonian, corresponding to eigenvalues E_1 and E_3 .

Let us measure the total energy of the system

| <i>possible outcome</i> | <i>probability</i> |
|-------------------------|---|
| E_1 | $\left \sqrt{\frac{2}{5}} \right ^2 = \frac{2}{5}$ |
| E_3 | $\left \sqrt{\frac{3}{5}} \right ^2 = \frac{3}{5}$ |

Interpretation. If we had 1000 copies of this particles in state ψ , then statistically $\frac{2}{5} \times 1000 = 400$ and $\frac{3}{5} \times 1000 = 600$ measurements of the total energy would yield E_1 and E_3 respectively. No other values (E_2 , E_4, \dots) will be measured.

If $\psi = \sum_n c_n \phi_n$, where $\hat{A}\phi_n = a_n \phi_n$, i.e. ϕ_n is the eigenfunction of an operator \hat{A} corresponding to the eigenvalue a_n , then

$$|c_n|^2 = \text{Pr}(A = a_n)$$

where $\text{Pr}(A = a_n)$ is the probability that a measurement of the corresponding physical quantity A will yield a_n .

Note.

In the example above $\hat{A} = \hat{H}$ (physical quantity is the total energy), $c_1 = \sqrt{\frac{2}{5}}$, $c_2 = \sqrt{\frac{3}{5}}$ and other c_n 's are zero.