

MP364 QUANTUM MECHANICS 2

Introduction

Quantum theory of angular momentum

Quantum theory of a particle in a central potential

- Hydrogen atom

- Three-dimensional isotropic harmonic oscillator (a model of atomic nucleus)

Non-relativistic quantum theory of electron spin

Addition of angular momenta

Stationary perturbation theory

(Time-dependent perturbation theory)

Systems of identical particles

REFERENCES

Claude Cohen-Tannoudji, Bernard Liu, and Franck Laloë

Quantum Mechanics I and II

John Wiley & Sons

Lecture Notes and **Problem Sets** - online access (no moodle!):

<http://www.thphys.nuim.ie/Notes/MP364/MP364.html>

REQUIREMENTS

The total mark of 100 points consists of:

Examination (constitutes 80% of the total mark):

duration: 120 minutes,

requirements: answer all questions in writing.

Maximum mark: 80 points.

Continuous Assessment (20% of the total mark):

quizzes / homework assignments.

Maximum mark: 20 points.

NOTE THAT CONTINUOUS ASSESSMENT IS AN INTEGRAL PART OF YOUR TOTAL MARK AND IS NOT APPLIED TO STUDENTS' ADVANTAGE

Section 0: FORMALISM OF QUANTUM MECHANICS

(From Cohen-Tannoudji, Chapters II & III)

Overview:

Postulates of quantum mechanics

- States of quantum mechanical systems
- Quantum operators and physical quantities
- Measurement postulates
- Time evolution of quantum systems

FIRST POSTULATE

At a fixed time t , the state of a physical system is defined by specifying a vector, or a ket, $|\psi(t)\rangle$ belonging to the state space \mathcal{H} .

The state space \mathcal{H} is a space of all possible states of a given physical system.

In quantum mechanics, this space is a **Hilbert space**.

What is a Hilbert space?

A complex vector space
with

- an inner product,
- a norm and a metric induced by the inner product, and is also
- complete as a metric space.

A Hilbert space is a complex inner product vector space that is also normed space and complete metric space with norm and metric induced by the inner product.

1) A complex vector space is a set of elements, called vectors (or **kets**), with an operation of **addition**, which for each pair of vectors $|\psi\rangle$ and $|\phi\rangle$ specifies a vector $|\psi\rangle + |\phi\rangle$, and an operation of **scalar multiplication**, which for each vector $|\psi\rangle$ and a number $c \in \mathbb{C}$ specifies a vector $c|\psi\rangle$ such that

a) $|\psi\rangle + |\phi\rangle = |\phi\rangle + |\psi\rangle$

b) $|\psi\rangle + (|\phi\rangle + |\chi\rangle) = (|\psi\rangle + |\phi\rangle) + |\chi\rangle$

c) there is a unique zero vector s.t. $|\psi\rangle + 0 = |\psi\rangle$

d) $c(|\psi\rangle + |\phi\rangle) = c|\psi\rangle + c|\phi\rangle$

e) $(c + d)|\psi\rangle = c|\psi\rangle + d|\psi\rangle$

f) $c(d|\psi\rangle) = (cd)|\psi\rangle$

g) $1 \cdot |\psi\rangle = |\psi\rangle$

h) $0 \cdot |\psi\rangle = 0$

We need a complex vector space to accommodate **the principle of superposition** and the related phenomena; recall for example an interference in the Young double slit experiment we have encountered in MP205 Vibrations & Waves.

Example: A set of N-tuples of complex numbers.

Example: Let us first consider a two-dimensional Hilbert space, \mathcal{H}^2 , like the one you encountered in MP363 Quantum Mechanics I when you studied a two level system of a particle with the spin 1/2.

The space represents all the states of the system and they all have the form

$$|\psi\rangle = c_{\uparrow}|\uparrow\rangle + c_{\downarrow}|\downarrow\rangle = \begin{pmatrix} c_{\uparrow} \\ c_{\downarrow} \end{pmatrix} = c_{\uparrow} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + c_{\downarrow} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

where c_{\uparrow} and c_{\downarrow} are complex numbers which we call **probability amplitudes**.

The probability amplitudes give us **probabilities**

$$p_{\uparrow} = c_{\uparrow}^* c_{\uparrow} = |c_{\uparrow}|^2$$

$$p_{\downarrow} = c_{\downarrow}^* c_{\downarrow} = |c_{\downarrow}|^2$$

that when we measure the spin of the particle we get spin \uparrow or spin \downarrow respectively.

The kets $|\uparrow\rangle$ and $|\downarrow\rangle$ are eigenstates of the operator \hat{S}_z corresponding to the eigenvalues $+\hbar/2$ and $-\hbar/2$. They serve as basis vectors or basis states, that is, they play a role in the Hilbert space similar to the role of orthogonal unit vectors \vec{i} , \vec{j} and \vec{k} in a three dimensional Euclidean space.

We need the inner product to be able to talk about orthogonality.

2. A complex vector space with an inner product.

The **inner product** assigns a complex number to a pair of kets $|\psi\rangle, |\phi\rangle \in \mathcal{H}$:

$$\langle\phi|\psi\rangle \in \mathbb{C}$$

A bra $\langle\phi|$ is the adjoint of a ket $|\phi\rangle$; we construct it as follows:

$$\begin{aligned} \text{if } & |\phi\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle, \\ \text{then } & \langle\phi| = c_1^*\langle\phi_1| + c_2^*\langle\phi_2| \end{aligned}$$

Properties:

complex conjugation $\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*$

sesquilinearity $\langle a_1\phi_1 + a_2\phi_2|\psi\rangle = a_1^*\langle\phi_1|\psi\rangle + a_2^*\langle\phi_2|\psi\rangle$

$$\langle\phi|c_1\psi_1 + c_2\psi_2\rangle = c_1\langle\phi|\psi_1\rangle + c_2\langle\phi|\psi_2\rangle$$

positive-definiteness $\langle\psi|\psi\rangle \geq 0$ where the equality holds iff $|\psi\rangle = 0$

3. Normed vector space and metric vector space

(a) **Norm** induced by the inner product:

$$\|\psi\| = \sqrt{\langle\psi|\psi\rangle} \quad \text{the norm of a state } |\psi\rangle$$

If the norm is 1, the state is said to be **normalized**.

If a given state $|\psi'\rangle$ is not normalized, $\|\psi'\| \neq 1$, then we have to normalize it, that is, to divide it by the norm. The normalized state is then

$$|\psi\rangle = \frac{|\psi'\rangle}{\sqrt{\langle\psi'|\psi'\rangle}}$$

Two vectors $|\phi\rangle$ and $|\psi\rangle$ are said to be **orthogonal** if their inner product is zero.

A set of normalized and mutually orthogonal vectors is an **orthonormal** set.

Example: **Basis vectors** form an **orthonormal set**.

We call the vectors $\{|\phi_1\rangle, |\phi_2\rangle, \dots\}$ a **basis vectors** or **basis states**, of \mathcal{H} iff

$$\begin{aligned}\text{span}\{|\phi_1\rangle, |\phi_2\rangle, \dots\} &= \mathcal{H} \\ \text{and } \langle\phi_i|\phi_j\rangle &= \delta_{ij}\end{aligned}$$

where δ_{ij} is the Kronecker delta-symbol:

$$\begin{aligned}\delta_{ij} &= 0 & \text{iff } i \neq j \\ \delta_{ij} &= 1 & \text{iff } i = j\end{aligned}$$

Example: A particle with spin 1/2:

Ket

$$|\psi\rangle = c_{\uparrow}|\uparrow\rangle + c_{\downarrow}|\downarrow\rangle = \begin{pmatrix} c_{\uparrow} \\ c_{\downarrow} \end{pmatrix} = c_{\uparrow} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + c_{\downarrow} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Bra: constructing the adjoint of $|\psi\rangle$

$$\langle\psi| = c_{\uparrow}^*\langle\uparrow| + c_{\downarrow}^*\langle\downarrow| = \begin{pmatrix} c_{\uparrow}^* & c_{\downarrow}^* \end{pmatrix} = c_{\uparrow}^* \begin{pmatrix} 1 & 0 \end{pmatrix} + c_{\downarrow}^* \begin{pmatrix} 0 & 1 \end{pmatrix}$$

Basis vectors: norm and orthogonality

$$\begin{aligned} \langle\uparrow|\uparrow\rangle &= \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1 & \langle\uparrow|\downarrow\rangle &= \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0 \\ \langle\downarrow|\uparrow\rangle &= \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0 & \langle\downarrow|\downarrow\rangle &= \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 1 \end{aligned}$$

Example: A particle with the spin 1/2: $|\psi\rangle = c_{\uparrow}|\uparrow\rangle + c_{\downarrow}|\downarrow\rangle = \begin{pmatrix} c_{\uparrow} \\ c_{\downarrow} \end{pmatrix}$

Norm

$$\begin{aligned} \|\psi\| &= \sqrt{\langle\psi|\psi\rangle} \\ \langle\psi|\psi\rangle &= (c_{\uparrow}^* \langle\uparrow| + c_{\downarrow}^* \langle\downarrow|) (c_{\uparrow} |\uparrow\rangle + c_{\downarrow} |\downarrow\rangle) \\ &= c_{\uparrow}^* c_{\uparrow} \langle\uparrow|\uparrow\rangle + c_{\uparrow}^* c_{\downarrow} \langle\uparrow|\downarrow\rangle + c_{\downarrow}^* c_{\uparrow} \langle\downarrow|\uparrow\rangle + c_{\downarrow}^* c_{\downarrow} \langle\downarrow|\downarrow\rangle \\ &= |c_{\uparrow}|^2 + |c_{\downarrow}|^2 = 1 \\ \|\psi\| &= 1 \end{aligned}$$

In matrix representation

$$\langle\psi|\psi\rangle = \begin{pmatrix} c_{\uparrow}^* & c_{\downarrow}^* \end{pmatrix} \begin{pmatrix} c_{\uparrow} \\ c_{\downarrow} \end{pmatrix} = |c_{\uparrow}|^2 + |c_{\downarrow}|^2 = 1$$

Note that the normalization condition translates as $|c_{\uparrow}|^2 + |c_{\downarrow}|^2 = p_{\uparrow} + p_{\downarrow} = 1$, that is, the probabilities of all mutually exclusive measurement results sum to unity.

(b) A **metric** is a map which assigns to each pair of vectors $|\psi\rangle, |\phi\rangle$ a scalar $\rho \geq 0$ s.t.

1. $\rho(|\psi\rangle, |\phi\rangle) = 0$ iff $|\psi\rangle = |\phi\rangle$;

2. $\rho(|\psi\rangle, |\phi\rangle) = \rho(|\phi\rangle, |\psi\rangle)$

3. $\rho(|\psi\rangle, |\chi\rangle) \leq \rho(|\psi\rangle, |\phi\rangle) + \rho(|\phi\rangle, |\chi\rangle)$ (triangle identity) We say that the metric is induced by the norm if

$$\rho(|\psi\rangle, |\phi\rangle) = \| |\psi\rangle - |\phi\rangle \|$$

So the Hilbert space is normed and it is a metric space. What else?

4. Hilbert space is also a complete metric space

We say that a metric space is complete if every Cauchy sequence of vectors, i.e.

$$\| |\psi_n\rangle - |\psi_m\rangle \| \rightarrow 0 \quad \text{as } m, n \rightarrow \infty$$

converges to a limit vector in the space.

We need this condition to be able to handle systems whose states are vectors in infinite-dimensional Hilbert spaces, i.e. systems with infinite degrees of freedom.

Representation of a quantum mechanical state

Can we be more concrete about quantum states? What really is a ket $|\psi\rangle$?

Let us say we have the two-dimensional Hilbert space \mathcal{H} with the basis

$$\mathcal{B} = \{|\uparrow\rangle, |\downarrow\rangle\}$$

We now consider a ket, or a vector, in this Hilbert space

$$|\psi\rangle \in \mathcal{H}$$

It is to be said that at this stage this vector is a very abstract entity.

We wish to make it more concrete by expressing the vector in **the representation given by the basis above \mathcal{B}** .

We will first introduce the **completeness relation** which is a useful way of expressing an identity operator on the Hilbert space.

In our specific example, the completeness relation has the form

$$|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| = \hat{1}$$

We use it to define the representations of $|\psi\rangle$

$$\begin{aligned} |\psi\rangle &= \hat{1} |\psi\rangle = (|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|) |\psi\rangle \\ &= |\uparrow\rangle\langle\uparrow|\psi\rangle + |\downarrow\rangle\langle\downarrow|\psi\rangle \\ &= \langle\uparrow|\psi\rangle |\uparrow\rangle + \langle\downarrow|\psi\rangle |\downarrow\rangle \\ &= c_{\uparrow} |\uparrow\rangle + c_{\downarrow} |\downarrow\rangle \end{aligned}$$

where the probability amplitudes are explicitly $c_{\uparrow} = \langle\uparrow|\psi\rangle$ and $c_{\downarrow} = \langle\downarrow|\psi\rangle$.

It is easy to verify in our case that the completeness relation is an identity operator using the matrix representation

$$|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hat{1}$$

More generally, the **completeness relation** is given as

$$\sum_i |\phi_i\rangle\langle\phi_i| = \hat{1}$$

where the sum goes over all basis vectors $\mathcal{B} = \{|\phi_1\rangle, |\phi_2\rangle, \dots\}$.

Our state can now be expanded into a specific superposition of the basis vectors $\{|\phi_i\rangle\}$

$$|\psi\rangle = \sum_i |\phi_i\rangle \underbrace{\langle\phi_i|\psi\rangle}_{\text{a number } c_i \in \mathbb{C}} = \sum_i c_i |\phi_i\rangle$$

What about a representation in a continuous case, for example a free particle?

The completeness relation:

We can choose as a suitable basis the set of eigenstates of the position operator \hat{X} , that is, the vectors satisfying

$$\hat{X} |x\rangle = x|x\rangle$$

where x is a position in one-dimensional space. Generalization to three dimensions is straightforward as we will see it later.

Since position is a continuous physical entity, the completeness relation is an integral

$$\int_{-\infty}^{\infty} |x\rangle\langle x| dx = \hat{1}$$

Coordinate representation

$$\begin{aligned} |\psi\rangle &\in \mathcal{H} \\ |\psi\rangle &= \int_{-\infty}^{\infty} |x\rangle \langle x|\psi\rangle dx \\ &= \int_{-\infty}^{\infty} \psi(x) |x\rangle dx \end{aligned}$$

$\{\psi(x)\}$ are coefficients of the expansion of $|\psi\rangle$ using the basis given by the eigenvectors of the operator \hat{X} , called wavefunction.

Inner product in coordinate representation

$$\langle \psi_1 | \psi_2 \rangle = \langle \psi_1 | \left(\int_{-\infty}^{\infty} |x\rangle \langle x| dx \right) | \psi_2 \rangle = \int_{-\infty}^{\infty} \langle \psi_1 | x \rangle \langle x | \psi_2 \rangle dx = \int_{-\infty}^{\infty} \psi_1^*(x) \psi_2(x) dx$$

Momentum representation

is constructed using the completeness relation based on the momentum eigenstates, satisfying the eigenvalue equation $\hat{P}|p\rangle = p|p\rangle$, as follows

$$\begin{aligned} |\psi\rangle &= \int_{-\infty}^{\infty} |p\rangle\langle p|\psi\rangle dp \\ &= \int_{-\infty}^{\infty} \psi(p) |p\rangle dp \end{aligned}$$

$\{\psi(p)\}$ are coefficients of the expansion of $|\psi\rangle$ using the basis given by the eigenvectors of the operator \hat{P} , called wavefunction in the momentum representation.

Inner product in momentum representation

$$\langle\psi_1|\psi_2\rangle = \langle\psi_1|\left(\int_{-\infty}^{\infty} |p\rangle\langle p| dp\right)|\psi_2\rangle = \int_{-\infty}^{\infty} \langle\psi_1|p\rangle\langle p|\psi_2\rangle dp = \int_{-\infty}^{\infty} \psi_1^*(p)\psi_2(p) dp$$

SECOND POSTULATE

Every measurable physical quantity \mathcal{A} is described by an operator \hat{A} acting on \mathcal{H} ; this operator is an observable.

An operator $\hat{A} : \mathcal{E} \rightarrow \mathcal{F}$ such that $|\psi'\rangle = \hat{A}|\psi\rangle$ for

$$\begin{aligned} |\psi\rangle &\in \underbrace{\mathcal{E}}_{\text{domain } D(\hat{A})} \\ \text{and } |\psi'\rangle &\in \underbrace{\mathcal{F}}_{\text{range } R(\hat{A})} \end{aligned}$$

Properties:

1. **Linearity:** $\hat{A} \sum_i c_i |\phi_i\rangle = \sum_i c_i \hat{A} |\phi_i\rangle$

2. **Equality:** $\hat{A} = \hat{B}$ iff $\hat{A}|\psi\rangle = \hat{B}|\psi\rangle$ and $D(\hat{A}) = D(\hat{B})$

3. **Sum:** $\hat{C} = \hat{A} + \hat{B}$ iff $\hat{C}|\psi\rangle = \hat{A}|\psi\rangle + \hat{B}|\psi\rangle$

4. **Product:** $\hat{C} = \hat{A}\hat{B}$ iff

$$\hat{C}|\psi\rangle = \hat{A}\hat{B}|\psi\rangle = \hat{A}(\hat{B}|\psi\rangle) = \hat{A}|\hat{B}\psi\rangle$$

Commutator and anticommutator

In contrast to numbers, a product of operators is generally **not** commutative, i.e.

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

For example: three vectors $|x\rangle$, $|y\rangle$ and $|z\rangle$ and two operators \hat{R}_x and \hat{R}_y such that:

$$\begin{aligned}\hat{R}_x|x\rangle &= |x\rangle, & \hat{R}_y|x\rangle &= -|z\rangle, \\ \hat{R}_x|y\rangle &= |z\rangle, & \hat{R}_y|y\rangle &= |y\rangle, \\ \hat{R}_x|z\rangle &= -|y\rangle, & \hat{R}_y|z\rangle &= |x\rangle\end{aligned}$$

then

$$\begin{aligned}\hat{R}_x\hat{R}_y|z\rangle &= \hat{R}_x|x\rangle = |x\rangle \neq \\ \hat{R}_y\hat{R}_x|z\rangle &= -\hat{R}_y|y\rangle = -|y\rangle\end{aligned}$$

Commutativity is inherent to **classical mechanics**. All physical quantities are represented by mathematical entities that are commutative. Moreover, specifying for example positions and momenta of a particle at a given time provides a complete description of its mechanical state.

In **quantum mechanics**, physical quantities are represented by operators that are **not commutative** in general. This **noncommutativity** is the very essence of quantum world and has important consequences like the Heisenberg uncertainty relation. Indeed, we can not obtain a sharp value of both position and momentum of a particle.

The most complete description of a quantum mechanical system is given by

the Complete Set of Commuting Observables or C.S.C.O.

An operator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is called **commutator**.

We say that \hat{A} and \hat{B} commute iff $[\hat{A}, \hat{B}] = 0$ in which case also $[f(\hat{A}), f(\hat{B})] = 0$.

Basic properties of commutators:

$$\begin{aligned}[\hat{A}, \hat{B}] &= -[\hat{B}, \hat{A}] \\ [\hat{A}, \hat{B} + \hat{C}] &= [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] \\ [\hat{A}, \hat{B}\hat{C}] &= [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]\end{aligned}$$

the **Jacobi identity**:

$$[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0$$

An operator $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$ is called **anticommutator**. Clearly

$$\{\hat{A}, \hat{B}\} = \{\hat{B}, \hat{A}\}$$

Types of operators (examples)

1. \hat{A} is **bounded** iff $\exists \beta > 0$ such that $\|\hat{A}|\psi\rangle\| \leq \beta \| |\psi\rangle \|$ for all $|\psi\rangle \in D(\hat{A})$.

In quantum mechanics, the domain $D(\hat{A})$ is the whole Hilbert space \mathcal{H} .

Infimum of β is called the **norm of the operator** \hat{A} .

2. Let \hat{A} be a bounded operator, then there is **an adjoint operator** \hat{A}^\dagger such that

$$\begin{aligned} \langle \psi_1 | \hat{A}^\dagger \psi_2 \rangle &= \langle \hat{A} \psi_1 | \psi_2 \rangle \\ \text{i.e.} \quad \langle \psi_1 | \hat{A}^\dagger \psi_2 \rangle &= \langle \psi_2 | \hat{A} \psi_1 \rangle^* \end{aligned}$$

for all $|\psi_1\rangle, |\psi_2\rangle \in \mathcal{H}$.

Properties:

$$\begin{aligned}\|\hat{A}^\dagger\| &= \|\hat{A}\| \\ (\hat{A}^\dagger)^\dagger &= \hat{A} \\ (\hat{A} + \hat{B})^\dagger &= \hat{A}^\dagger + \hat{B}^\dagger \\ (\hat{A}\hat{B})^\dagger &= \hat{B}^\dagger\hat{A}^\dagger \text{ (the order changes)} \\ (\lambda\hat{A})^\dagger &= \lambda^*\hat{A}^\dagger\end{aligned}$$

How can we construct an adjoint?

If we have an operator in a matrix representation, so it is a matrix, then

$$\hat{A}^\dagger = (A^T)^* = \text{transpose and complex conjugation}$$

3. \hat{A} is called **hermitian** or **selfadjoint** if $\hat{A}^\dagger = \hat{A}$, or $\langle \hat{A}\phi|\psi\rangle = \langle \phi|\hat{A}\psi\rangle$.

This is the property of quantum observables!

Their eigenvalues are real numbers, e.g. $\hat{X}|x\rangle = x|x\rangle$ or $\hat{H}|E\rangle = E|E\rangle$

4. \hat{A} is **positive** if $\langle \psi|\hat{A}|\psi\rangle \geq 0$ for all $|\psi\rangle \in \mathcal{H}$

5. Let \hat{A} be an operator. If there exists an operator \hat{A}^{-1} such that $\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = \hat{1}$ (identity operator) then \hat{A}^{-1} is called an **inverse operator** to \hat{A}

Properties:

$$\begin{aligned}(\hat{A}\hat{B})^{-1} &= \hat{B}^{-1}\hat{A}^{-1} \\ (\hat{A}^\dagger)^{-1} &= (\hat{A}^{-1})^\dagger\end{aligned}$$

6. an operator \hat{U} is called **unitary** if $\hat{U}^\dagger = \hat{U}^{-1}$, i.e. $\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \hat{1}$.

Example: Quantum evolution operator

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}\hat{H}t}|\psi(0)\rangle = \hat{U}|\psi(0)\rangle$$

7. An operator \hat{P} satisfying $\hat{P} = \hat{P}^\dagger = \hat{P}^2$ is a **projection operator** or **projector**
e.g. if $|\psi_k\rangle$ is a normalized vector then

$$\hat{P}_k = |\psi_k\rangle\langle\psi_k|$$

is the projector onto one-dimensional space spanned by all vectors linearly dependent on $|\psi_k\rangle$.

Composition of operators (by example)

1. Direct sum

If you can write an operator as

$$\hat{A} = \begin{pmatrix} b_{11} & b_{12} & 0 & 0 & 0 \\ b_{21} & b_{22} & 0 & 0 & 0 \\ 0 & 0 & c_{11} & c_{12} & c_{13} \\ 0 & 0 & c_{21} & c_{22} & c_{23} \\ 0 & 0 & c_{31} & c_{32} & c_{33} \end{pmatrix}$$

then it is a direct sum $\hat{A} = \hat{B} \oplus \hat{C}$ where \hat{B} acts on \mathcal{H}_B (2 dimensional) and \hat{C} acts on \mathcal{H}_C (3 dimensional)

$$\hat{B} = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \quad \text{and} \quad \hat{C} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix}$$

and \hat{A} acts on the direct sum of Hilber spaces $\mathcal{H}_B \oplus \mathcal{H}_C$.

Properties:

$$\begin{aligned}\text{Tr}(\hat{B} \oplus \hat{C}) &= \text{Tr}(\hat{B}) + \text{Tr}(\hat{C}) \\ \det(\hat{B} \oplus \hat{C}) &= \det(\hat{B}) \det(\hat{C})\end{aligned}$$

Applications: Addition of angular momentum

A system of two spin half particles is described by a ket in 4-dimensional Hilbert space

$$\mathcal{H} = \mathcal{H}_{j=0} \oplus \mathcal{H}_{j=1}$$

where $\mathcal{H}_{j=0}$ is spanned by a singlet state and $\mathcal{H}_{j=1}$ by a triplet state.

2. Direct product $\hat{A} = \hat{B} \otimes \hat{C}$:

Let $|\psi\rangle \in \mathcal{H}_B$, $|\phi\rangle \in \mathcal{H}_C$, $|\chi\rangle \in \mathcal{H}_B \otimes \mathcal{H}_C$, then

$$\hat{A} |\chi\rangle = (\hat{B} \otimes \hat{C})(|\psi\rangle \otimes |\phi\rangle) = \hat{B}|\psi\rangle \otimes \hat{C}|\phi\rangle = \hat{B}|\psi\rangle \hat{C}|\phi\rangle$$

$$\hat{A} = \begin{pmatrix} b_{11}c_{11} & b_{11}c_{12} & b_{11}c_{13} & b_{12}c_{11} & b_{12}c_{12} & b_{12}c_{13} \\ b_{11}c_{21} & b_{11}c_{22} & b_{11}c_{23} & b_{12}c_{21} & b_{12}c_{22} & b_{12}c_{23} \\ b_{11}c_{31} & b_{11}c_{32} & b_{11}c_{33} & b_{12}c_{31} & b_{12}c_{32} & b_{12}c_{33} \\ b_{21}c_{11} & b_{21}c_{12} & b_{21}c_{13} & b_{22}c_{11} & b_{22}c_{12} & b_{22}c_{13} \\ b_{21}c_{21} & b_{21}c_{22} & b_{21}c_{23} & b_{22}c_{21} & b_{22}c_{22} & b_{22}c_{23} \\ b_{21}c_{31} & b_{21}c_{32} & b_{21}c_{33} & b_{22}c_{31} & b_{22}c_{32} & b_{22}c_{33} \end{pmatrix}$$

Eigenvalues and eigenvectors

Solving a quantum mechanical system means to find the eigenvalues and eigenvectors of the complete set of commuting observables (C.S.C.O.)

1. The eigenvalue equation

$$\hat{A}|\psi_\alpha\rangle = \underbrace{\alpha}_{\text{eigenvalue}} \underbrace{|\psi_\alpha\rangle}_{\text{eigenvector}}$$

If $n > 1$ vectors satisfy the eigenvalue equation for the same eigenvalue α , we say the eigenvalue is **n -fold degenerate**.

2. The eigenvalues of a self-adjoint operator \hat{A} , which are observables and represent physical quantities, are real numbers

$$\alpha\langle\psi_\alpha|\psi_\alpha\rangle = \langle\psi_\alpha|\hat{A}\psi_\alpha\rangle = \langle\hat{A}\psi_\alpha|\psi_\alpha\rangle^* = \alpha^*\langle\psi_\alpha|\psi_\alpha\rangle \Rightarrow \alpha = \alpha^* \in \mathbb{R}$$

3. Eigenvectors of self-adjoint operators corresponding to distinct eigenvalues are orthogonal.

Proof: If $\beta \neq \alpha$ is also an eigenvalue of \hat{A} then

$$\langle \psi_\alpha | \hat{A} \psi_\beta \rangle = \beta \langle \psi_\alpha | \psi_\beta \rangle$$

and also

$$\langle \psi_\alpha | \hat{A} \psi_\beta \rangle = \langle \psi_\beta | \hat{A} \psi_\alpha \rangle^* = \alpha^* \langle \psi_\beta | \psi_\alpha \rangle^* = \alpha \langle \psi_\alpha | \psi_\beta \rangle$$

which implies

$$\langle \psi_\alpha | \psi_\beta \rangle = 0$$

4. Matrix representation

Operator is uniquely defined by its action on the basis vectors of the Hilbert space.

Let $\mathcal{B} = \{|\psi_j\rangle\}$ be a basis of a finite-dimensional \mathcal{H}

$$\begin{aligned}\hat{A}|\psi_j\rangle &= \sum_k |\psi_k\rangle \langle \psi_k | \hat{A} | \psi_j \rangle \\ &= \sum_k A_{kj} |\psi_k\rangle\end{aligned}$$

where $A_{kj} = \langle \psi_k | \hat{A} | \psi_j \rangle$ are the matrix elements of the operator \hat{A} in the matrix representation given by the basis \mathcal{B} .

For practical calculations

$$\hat{A} = \sum_{kj} |\psi_k\rangle \langle \psi_k | \hat{A} | \psi_j \rangle \langle \psi_j | = \sum_{kj} A_{kj} |\psi_k\rangle \langle \psi_j |$$

5. Spectral decomposition

Assume that the eigenvectors of \hat{A} define a basis $\mathcal{B} = \{|\psi_j\rangle\}$,
then $A_{kj} = \langle\psi_k|\hat{A}|\psi_j\rangle = \alpha_j\delta_{kj}$.

Operator in this basis is a diagonal matrix with eigenvalues on the diagonal

$$\begin{aligned}\hat{A} &= \sum_{kj} A_{kj} |\psi_k\rangle\langle\psi_j| \\ &= \sum_j \alpha_j |\psi_j\rangle\langle\psi_j| \\ &= \sum_j \alpha_j \hat{E}_j\end{aligned}$$

\hat{E}_j is a projector onto 1-dim. space spanned by $|\psi_j\rangle \Rightarrow$ Spectral decomposition!

Generalization to the continuous spectrum

$$\begin{aligned}\hat{A}|\alpha\rangle &= \alpha|\alpha\rangle \\ \langle\alpha'|\alpha\rangle &= \delta(\alpha - \alpha')\end{aligned}$$

δ -function [Cohen-Tannoudji II Appendix II]

Spectral decomposition

$$\hat{A} = \int_{\alpha_{\min}}^{\alpha_{\max}} \alpha|\alpha\rangle\langle\alpha|d\alpha$$

Completeness relation

$$\int_{\alpha_{\min}}^{\alpha_{\max}} |\alpha\rangle\langle\alpha|d\alpha = \hat{1}$$

Wavefunction

$$\psi(\alpha) = \langle\alpha|\psi\rangle$$

Functions of operators

Generally, we need to use the spectral decomposition of the operator

$$\hat{A} = \sum_j \alpha_j |\psi_j\rangle\langle\psi_j|$$

where $|\psi_j\rangle$ is the eigenvector of \hat{A} corresponding to the eigenvalue α_j :

$$\hat{A} |\psi_j\rangle = \alpha_j |\psi_j\rangle.$$

Then the function of \hat{A} is given as

$$f(\hat{A}) = \sum_j f(\alpha_j) |\psi_j\rangle\langle\psi_j|$$

Also, $\hat{A}^2 = \hat{A}\hat{A}$, then $\hat{A}^n = \hat{A}\hat{A}^{n-1}$ and if a function $f(\xi) = \sum_n a_n \xi^n$, then by the function of an operator $f(\hat{A})$ we mean

$$f(\hat{A}) = \sum_n a_n \hat{A}^n$$

e.g.

$$e^{\hat{A}} = \sum_{n=0}^{\infty} \frac{1}{n!} \hat{A}^n$$

Inner product

$$\langle \psi_1 | \psi_2 \rangle = \int_{\alpha_{\min}}^{\alpha_{\max}} \psi_1^*(\alpha) \psi_2(\alpha) d\alpha$$

Coordinate and momentum operators

In coordinate representation (x -representation)

$$\hat{X} = \int_{-\infty}^{\infty} x |x\rangle \langle x| dx \quad \text{spectral decomposition}$$

and $\int_{-\infty}^{\infty} |x\rangle \langle x| dx = \hat{1} \quad \text{completeness relation}$

$$|\psi\rangle = \int_{-\infty}^{\infty} |x\rangle \langle x|\psi\rangle dx = \int_{-\infty}^{\infty} \psi(x) |x\rangle dx$$

What about momentum operator \hat{P} ?

It has to satisfy the canonical commutation relation

$$\begin{aligned} [\hat{X}, \hat{P}] |\psi\rangle &= \hat{X}\hat{P}|\psi\rangle - \hat{P}\hat{X}|\psi\rangle \\ &= i\hbar|\psi\rangle \end{aligned}$$

which in **coordinate representation** is

$$x\hat{P}^{(x)}\psi(x) - \hat{P}^{(x)}x\psi(x) = i\hbar\psi(x)$$

This is satisfied by

$$\hat{P}^{(x)} = -i\hbar\frac{\partial}{\partial x}$$

In **momentum representation**

$$\begin{aligned} \mathcal{B} = \{|p\rangle\} : \quad \hat{P} &= \int_{-\infty}^{\infty} p|p\rangle\langle p| dp \\ \text{and} \quad \hat{X} &= i\hbar\frac{\partial}{\partial p} \end{aligned}$$

More on coordinate and momentum representation

Coordinate representation

$$\hat{X} = \int_{-\infty}^{\infty} x|x\rangle\langle x| dx \quad \hat{X}|x\rangle = x|x\rangle$$
$$\hat{P}^{(x)} = -i\hbar \frac{\partial}{\partial x} \quad \Leftarrow \quad [\hat{X}, \hat{P}] = i\hbar$$

For all $p \in \mathbb{R}$, there is a solution to the eigenvalue equation

$$-i\hbar \frac{d}{dx} \psi_p(x) = p\psi_p(x)$$

where $\psi_p(x)$ is **the eigenstate of the momentum operator in coordinate representation** corresponding to eigenvalue p

$$\hat{P}|p\rangle = p|p\rangle \quad |p\rangle = \int_{-\infty}^{\infty} |x\rangle\langle x|p\rangle dx = \int_{-\infty}^{\infty} \psi_p(x)|x\rangle dx$$

and every solution depends linearly on function

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}px} = \langle x|p\rangle$$

which satisfies the normalization condition

$$\int_{-\infty}^{\infty} \psi_{p'}^*(x) \psi_p(x) dx = \delta(p - p')$$

Similarly

$$\int_{-\infty}^{\infty} \psi_p^*(x') \psi_p(x) dp = \delta(x - x')$$

Momentum representation

$$\hat{P} = \int_{-\infty}^{\infty} p |p\rangle \langle p| dp$$

The completeness relation

$$\int_{-\infty}^{\infty} |p\rangle \langle p| dp = \hat{1}$$

$$|\phi\rangle = \int_{-\infty}^{\infty} |p\rangle \langle p|\phi\rangle dp = \int_{-\infty}^{\infty} \overbrace{\phi^{(p)}(p)}^{\text{momentum representation}} |p\rangle dp$$

How is the wavefunction $\phi^{(p)}(p)$, which describes the ket $|\phi\rangle$ in the momentum representation, related to $\phi(x)$ which describes the same vector in the coordinate representation?

$$\phi^{(p)}(p) = \int_{-\infty}^{\infty} \langle p|x\rangle \langle x|\phi\rangle dx = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-\frac{i}{\hbar}px} \phi(x) dx$$

$\phi^{(p)}(p)$ is the Fourier transform of $\phi(x)$

$\phi(x)$ is the inverse F.T. of $\phi^{(p)}(p)$

$$\phi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{+\frac{i}{\hbar}px} \phi^{(p)}(p) dp$$

(Cohen-Tannoudji Q.M. II Appendix I)

The Parseval-Plancharel formula

$$\int_{-\infty}^{\infty} \phi^*(x)\psi(x) dx = \int_{-\infty}^{\infty} \phi^{(p)*}(p)\psi^{(p)}(p) dp$$

F.T. in 3 dimensions:

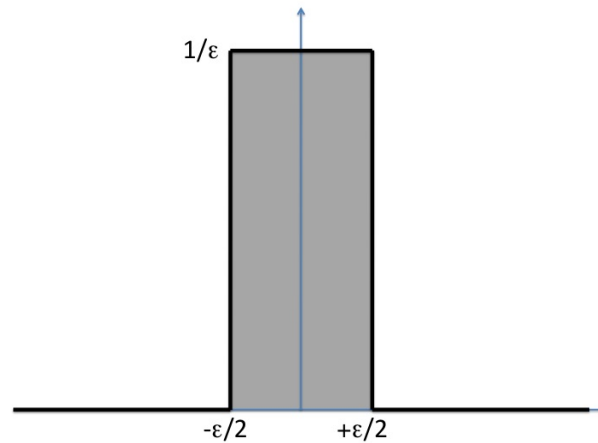
$$\phi^{(p)}(\vec{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}} \phi(\vec{r}) d^3r$$

δ -"function"

1. Definition and principal properties

Consider $\delta^\epsilon(x)$:

$$\delta^\epsilon(x) = \begin{cases} \frac{1}{\epsilon} & \text{for } -\frac{\epsilon}{2} \leq x \leq \frac{\epsilon}{2} \\ 0 & \text{for } |x| > \frac{\epsilon}{2} \end{cases}$$



and evaluate $\int_{-\infty}^{\infty} \delta^\epsilon(x) f(x) dx$ (where $f(x)$ is an arbitrary function defined at $x = 0$)
if ϵ is very small ($\epsilon \rightarrow 0$)

$$\begin{aligned} \int_{-\infty}^{\infty} \delta^\epsilon(x) f(x) dx &\approx f(0) \int_{-\infty}^{\infty} \delta^\epsilon(x) dx \\ &= f(0) \end{aligned}$$

the smaller the ϵ , the better the approximation.

For the limit $\epsilon = 0$, $\delta(x) = \lim_{\epsilon \rightarrow 0} \delta^\epsilon(x)$.

$$\int_{-\infty}^{\infty} \delta(x) f(x) dx = f(0)$$

More generally

$$\int_{-\infty}^{\infty} \delta(x - x_0) f(x) dx = f(x_0)$$

Properties

(i) $\delta(-x) = \delta(x)$

(ii) $\delta(cx) = \frac{1}{|c|}\delta(x)$

and more generally

$$\delta[g(x)] = \sum_j \frac{1}{|g'(x_j)|} \delta(x - x_j)$$

$\{x_j\}$ simple zeroes of $g(x)$ i.e. $g(x_j) = 0$ and $g'(x_j) \neq 0$

(iii) $x\delta(x - x_0) = x_0\delta(x - x_0)$

and in particular $x\delta(x) = 0$

and more generally $g(x)\delta(x - x_0) = g(x_0)\delta(x - x_0)$

(iv)
$$\int_{-\infty}^{\infty} \delta(x - y)\delta(x - z) dx = \delta(y - z)$$

The δ -"function" and the Fourier transform

$$\begin{aligned}\psi^{(p)}(p) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-\frac{i}{\hbar}px} \psi(x) dx \\ \psi(x) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}px} \psi^{(p)}(p) dp\end{aligned}$$

The Fourier transform $\delta^{(p)}(p)$ of $\delta(x - x_0)$:

$$\begin{aligned}\delta^{(p)}(p) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-\frac{i}{\hbar}px} \delta(x - x_0) dx \\ &= \frac{1}{\sqrt{2\pi\hbar}} e^{-\frac{i}{\hbar}px_0}\end{aligned}$$

The inverse F.T.

$$\begin{aligned}\delta(x - x_0) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}px} \delta^{(p)}(p) dp \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}px} \frac{1}{\sqrt{2\pi\hbar}} e^{-\frac{i}{\hbar}px_0} dp \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}p(x-x_0)} dp \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x_0)} dk\end{aligned}$$

Derivative of $\delta(x)$

$$\begin{aligned}\int_{-\infty}^{\infty} \delta'(x - x_0) f(x) dx &= \\ - \int_{-\infty}^{\infty} \delta(x - x_0) f'(x) dx &= -f'(x_0)\end{aligned}$$

THIRD POSTULATE
(Measurement I)

The only possible result of the measurement of a physical quantity \mathcal{A} is one of the eigenvalues of the corresponding observable \hat{A} .

FOURTH POSTULATE (Measurement II)

1. a discrete non-degenerate spectrum:

When the physical quantity \mathcal{A} is measured on a system in the normalized state $|\psi\rangle$, the probability $\mathcal{P}(a_n)$ of obtaining the non-degenerate eigenvalue a_n of the corresponding physical observable \hat{A} is

$$\mathcal{P}(a_n) = |\langle u_n | \psi \rangle|^2$$

where $|u_n\rangle$ is the normalised eigenvector of \hat{A} associated with the eigenvalue a_n .

2. a discrete spectrum:

$$\mathcal{P}(a_n) = \sum_{i=1}^{g_n} |\langle u_n^i | \psi \rangle|^2$$

where g_n is the degree of degeneracy of a_n and $\{|u_n^i\rangle\}$ ($i = 1, \dots, g_n$) is an orthonormal set of vectors which forms a basis in the eigenspace \mathcal{H}_n associated with the eigenvalue a_n of the observable \hat{A} .

3. a continuous spectrum:

the probability $d\mathcal{P}(\alpha)$ of obtaining result included between α and $\alpha + d\alpha$ is

$$d\mathcal{P}(\alpha) = |\langle v_\alpha | \psi \rangle|^2 d\alpha$$

where $|v_\alpha\rangle$ is the eigenvector corresponding to the eigenvalue α of the observable \hat{A} .

FIFTH POSTULATE (Measurement III)

If the measurement of the physical quantity \mathcal{A} on the system in the state $|\psi\rangle$ gives the result a_n , the state of the system immediately after the measurement is the normalized projection

$$\frac{\hat{P}_n|\psi\rangle}{\sqrt{\langle\psi|\hat{P}_n|\psi\rangle}} = \frac{\hat{P}_n|\psi\rangle}{\|\hat{P}_n|\psi\rangle\|}$$

of $|\psi\rangle$ onto the eigensubspace associated with a_n .

SIXTH POSTULATE (Time Evolution)

The time evolution of the state vector $|\psi(t)\rangle$ is governed by the Schrödinger equation

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

where $\hat{H}(t)$ is the observable associated with the total energy of the system.

Classically

$$H(\vec{r}, \vec{p}) = \frac{\vec{p}^2}{2m} + V(\vec{r})$$

Quantum mechanics

$$\left. \begin{array}{l} \vec{r} \rightarrow \hat{\vec{R}} \\ \vec{p} \rightarrow \hat{\vec{P}} \end{array} \right\} \hat{H} = \frac{\hat{\vec{P}}^2}{2m} + V(\hat{\vec{R}})$$

Canonical quantization (in the coordinate rep.)

$$\begin{aligned}\hat{\vec{R}} &\rightarrow \vec{r} \\ \hat{P}_i &\rightarrow -i\hbar \frac{\partial}{\partial x_i} = (-i\hbar \vec{\nabla})_i\end{aligned}$$

$$\Rightarrow \hat{H} = \underbrace{-\frac{\hbar^2}{2m} \nabla^2}_{\text{kinetic energy}} + \underbrace{V(\vec{r})}_{\text{potential energy}}$$

Formal solution of the Schrödinger equation gives the **quantum evolution operator**:

$$\begin{aligned} i\hbar \frac{d}{dt} |\psi(t)\rangle &= \hat{H} |\psi(t)\rangle \\ \Rightarrow \int_0^t \frac{d|\psi(t')\rangle}{|\psi(t')\rangle} &= -\frac{i}{\hbar} \int_0^t \hat{H} dt' \end{aligned}$$

By integrating, we get the evolution operator

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar} \int_0^t \hat{H}(t') dt'} |\psi(0)\rangle = \hat{U}(t) |\psi(0)\rangle$$

Its form is particularly simple if the Hamiltonian is time independent:

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar} \hat{H} t} |\psi(0)\rangle = \hat{U}(t) |\psi(0)\rangle$$