MP463 QUANTUM MECHANICS

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.maynoothuniversity.ie/Notes/MP463/MP463.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) $1.|\psi\rangle = |\psi\rangle$

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

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:

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

Properties:

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

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

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

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

3. <u>Normed vector space and metric vector space</u>

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

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

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

If a given state $|\psi'\rangle$ is not normalized, $\left\|\psi'\right\| \neq 1$, 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 $\{|\phi_1\rangle, |\phi_2\rangle, \ldots\}$ a **basis vectors** or **basis states**, of $\mathcal{H}$ iff

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

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

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

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

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

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

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

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

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.

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

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 $\mathcal{B} = \{|\phi_1\rangle, |\phi_2\rangle \ldots\}$.

Our state can now be expanded into a 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?

<u>The completeness relation:</u>
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

$$\int_{-\infty}^{\infty} |x\rangle\langle x|\,\mathrm{d}x \quad = \quad \hat{1}$$

Coordinate representation

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

$\{\psi(x)\}$ 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

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

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

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

$\{\psi(p)\}$ 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

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

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

$$|\psi\rangle \in \underbrace{\mathcal{E}}_{\text{domain } D(\hat{A})}$$

and $$|\psi'\rangle \in \underbrace{\mathcal{F}}_{\text{range } R(\hat{A})}$$

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

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

5. **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

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

e.g.

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

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

$$\hat{R}_x\hat{R}_y|z\rangle = \hat{R}_x|x\rangle = |x\rangle \quad \neq$$
$$\hat{R}_y\hat{R}_x|z\rangle = -\hat{R}_y|y\rangle = -|y\rangle$$

An operator $\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is called **commutator**.
We say that $\hat{A}$ and $\hat{B}$ commute iff $\left[\hat{A}, \hat{B}\right] = 0$ in which case also $\left[f(\hat{A}), f(\hat{B})\right] = 0$.

Basic properties of commutators:

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

the **Jacobi identity**:

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

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

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

Types of operators (examples)

1. $\hat{A}$ is **bounded** iff $\exists \beta > 0$ such that $\left\| \hat{A}|\psi\rangle \right\| \leq \beta \, \||\psi\rangle\|$ 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:

$$\left\|\hat{A}^\dagger\right\| = \left\|\hat{A}\right\|$$

$$\left(\hat{A}^\dagger\right)^\dagger = \hat{A}$$

$$\left(\hat{A}+\hat{B}\right)^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$$

$$\left(\hat{A}\hat{B}\right)^\dagger = \hat{B}^\dagger\hat{A}^\dagger \text{(the order changes)}$$

$$\left(\lambda\hat{A}\right)^\dagger = \lambda^*\hat{A}^\dagger$$

How can we construct an adjoint?

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

$$\hat{A}^\dagger = \left(A^{\mathrm{T}}\right)^* = \textbf{transpose and complex conjugation}$$

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:

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

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** $\hat{A} = \hat{B} \oplus \hat{C}$

$\hat{B}$ acts on $\mathcal{H}_B$ (2 dimensional) and $\hat{C}$ acts on $\mathcal{H}_C$ (3 dimensional)

Let

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

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

Acts on $\mathcal{H}_B \oplus \mathcal{H}_C$

Properties:

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

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

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

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

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.**

<u>Proof:</u> 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 $\mathcal{B} = \left\{|\psi_j\rangle\right\}$ 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 $\mathcal{B} = \left\{|\psi_j\rangle\right\}$,
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

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

δ-function [Cohen-Tannoudji II Appendix II]

Spectral decomposition

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

Completeness relation

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

Wavefunction

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

Inner product

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

Coordinate and momentum operators

In coordinate representation (x-representation)

$$\hat{X} = \int_{-\infty}^{\infty} x|x\rangle\langle x|\;\mathrm{d}x \qquad \text{spectral decomposition}$$

$$\text{and} \int_{-\infty}^{\infty} |x\rangle\langle x|\;\mathrm{d}x = \hat{1} \qquad \text{completeness relation}$$

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

What about momentum operator $\hat{P}$?
It has to satisfy the canonical commutation relation

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

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**

$$\mathcal{B} = \{|p\rangle\} : \qquad \hat{P} = \int_{-\infty}^{\infty} p|p\rangle\langle p| \, \mathrm{d}p$$

$$\text{and} \qquad \hat{X} = i\hbar\frac{\partial}{\partial p}$$

More on coordinate and momentum representation

Coordinate representation

$$\hat{X} = \int_{-\infty}^{\infty} x|x\rangle\langle x| \, \mathrm{d}x \qquad \hat{X}|x\rangle = x|x\rangle$$

$$\hat{P}^{(x)} = -i\hbar\frac{\partial}{\partial x} \quad \Leftarrow \quad \left[\hat{X}, \hat{P}\right] = i\hbar$$

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

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

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

$$\hat{P}|p\rangle = p|p\rangle \qquad |p\rangle = \int_{-\infty}^{\infty} |x\rangle\langle x|p\rangle \, \mathrm{d}x = \int_{-\infty}^{\infty} \psi_p(x)|x\rangle \, \mathrm{d}x$$

and every solution depends linearly on function

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

which satisfies the normalization condition

$$\int_{-\infty}^{\infty} \psi_{p'}^*(x)\psi_p(x)\,\mathrm{d}x \quad = \quad \delta\left(p - p'\right)$$

Similarly

$$\int_{-\infty}^{\infty} \psi_p^*\left(x'\right)\psi_p(x)\,\mathrm{d}p \quad = \quad \delta\left(x - x'\right)$$

Momentum representation

$$\hat{P} \;=\; \int_{-\infty}^{\infty} p|p\rangle\langle p| \,\mathrm{d}p$$

The completeness relation

$$\int_{-\infty}^{\infty} |p\rangle\langle p| \,\mathrm{d}p \;=\; \hat{1}$$

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

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?

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

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

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

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

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

The Parseval-Plancharel formula

$$\int_{-\infty}^{\infty} \phi^*(x)\psi(x)\, \mathrm{d}x = \int_{-\infty}^{\infty} \phi^{(p)*}(p)\psi^{(p)}(p)\, \mathrm{d}p$$

F.T. in 3 dimensions:

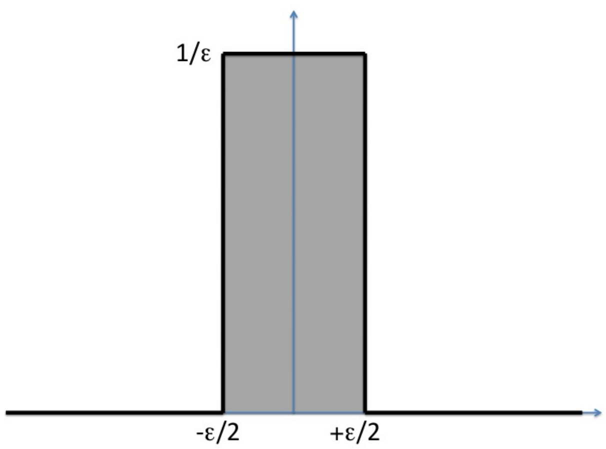
$$\phi^{(p)}(\vec{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}} \phi(\vec{r})\, \mathrm{d}^3 r$$

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 $\int_{-\infty}^{\infty} \delta^{\epsilon}(x) f(x)\, \mathrm{d}x$ (where $f(x)$ is an arbitrary function defined at $x = 0$) if ϵ is very small ($\epsilon \to 0$)

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

the smaller the ϵ, the better the approximation.

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

$$\int_{-\infty}^{\infty} \delta(x) f(x)\, \mathrm{d}x = f(0)$$

More generally

$$\int_{-\infty}^{\infty} \delta(x - x_0) f(x)\, \mathrm{d}x = f(x_0)$$

Properties

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

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

and more generally

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

$\{x_j\}$ 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 $g(x)\delta(x - x_0) = g(x_0)\delta(x - x_0)$

$$\text{(iv)} \qquad \int_{-\infty}^{\infty} \delta(x-y)\delta(x-z)\, \mathrm{d}x = \delta(y-z)$$

The δ-"function" and the Fourier transform

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

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

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

The inverse F.T.

$$
\begin{aligned}
\delta\left(x-x_0\right) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}px} \delta^{(p)}(p)\,\mathrm{d}p \\
&= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}px} \frac{1}{\sqrt{2\pi\hbar}} e^{-\frac{i}{\hbar}px_0}\,\mathrm{d}p \\
&= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}p(x-x_0)}\,\mathrm{d}p \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x_0)}\,\mathrm{d}k
\end{aligned}
$$

Derivative of $\delta(x)$

$$
\begin{aligned}
&\int_{-\infty}^{\infty} \delta'\left(x-x_0\right) f(x)\,\mathrm{d}x = \\
&-\int_{-\infty}^{\infty} \delta\left(x-x_0\right) f'(x)\,\mathrm{d}x = -f'\left(x_0\right)
\end{aligned}
$$

THIRD POSTULATE
(Measurement I)

The only possible result of the measurement of a physical quantity $\mathscr{A}$ 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:

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

where g_n is the degree of degeneracy of a_n and $\{|u_n^i\rangle\}$ $(i = 1, \ldots, g_n)$ 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 $\mathrm{d}\mathcal{P}(\alpha)$ of obtaining result included between α and $\alpha + \mathrm{d}\alpha$ is

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

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 $\mathscr{A}$ 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

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

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

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

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

—————————-

Classically

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

Quantum mechanics

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

Canonical quantization (in the coordinate rep.)

$$\hat{\vec{R}} \rightarrow \vec{r}$$

$$\hat{P}_i \rightarrow -i\hbar\frac{\partial}{\partial x_i} = \left(-i\hbar\vec{\nabla}\right)_i$$

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

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

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

By integrating, we get the evolution operator

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

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

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