IV. Mathematical Structure of QM and Essential Math to Move on – Part 1

Let's take stock of what we have...

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

- For $U = U(x)$ only,

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

  - Solutions $\underbrace{\psi_E(x)}_{\text{state of definite energy } E}$ and $\underbrace{E}_{\text{allowed values of energy of system}}$ (many pairs of them)

  $\psi_E(x)$ evolves as $\psi_E(x)\underbrace{e^{-iEt/\hbar}}_{\text{time part of that value of } E}$

- $|\Psi(x,t)|^2 dx$ = Prob. of finding particle in interval x to $x+dx$ at time t

A. Motivation

TISE $\quad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + U(x)\psi(x) = E\psi(x)$

Rewrite as: $\underbrace{\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\right]}_{\text{a mathematical operation that acts on a function that appears right after it}}\psi(x) = E\psi(x)$

Often written as: $\boxed{\hat{H}\psi = E\psi}$ (TISE)

- What is $\hat{H}$?
- Where is its root?
- What is the math structure behind TISE?

Using $\hat{H}$, TDSE becomes $\boxed{\hat{H}\psi = i\hbar\frac{\partial}{\partial t}\psi}$

B. Operators: A practical Approach

Let $\hat{A}$ represent a mathematical operation that acts on whatever comes behind it

Generally,

$$\underbrace{\hat{A}}_{\text{"operator"}} f(x) = g(x)$$

returns some function $g(x)$

$\hat{A}$ acts on $f(x)$

E.g. $\hat{A}$ (in words): "take derivative w.r.t. x"

$\hat{A} = \dfrac{d}{dx}$; if $f(x) = \sin kx$ then $\hat{A} f(x) = \overbrace{k \cos kx}^{g(x)}$

if $f(x) = e^{ikx}$ then $\hat{A} e^{ikx} = \underbrace{ik e^{ikx}}_{g(x)}$

e.g. $\hat{A} = \underbrace{\left[\frac{d^2}{dx^2} + 3\frac{d}{dx} + 4\right]}_{\text{takes in a } f(x) \text{ and do several things on it}}$

several operators put together

$$\hat{A}\underbrace{x^6}_{f(x)} = \underbrace{30x^4 + 18x^5 + 4x^6}_{g(x)}$$

e.g. $\hat{A} = \int_0^1 dx$ [What is this? Take in $f(x)$ and do $\int_0^1 dx\, f(x)$]

$$\hat{A}\underbrace{x^6}_{f(x)} = \int_0^1 dx\, x^6 = \frac{1}{7}x^7\Big|_0^1 = \underbrace{\frac{1}{7}}_{g(x)}$$

[although x-independent in this example] e.g. $\hat{A} = \text{SQRT}$ (take in $f(x)$ and take square root)

$$\hat{A}\,\underbrace{x^6}_{f(x)} = (x^6)^{1/2} = \underbrace{x^3}_{g(x)}$$

e.g. $\hat{A} = \frac{\hbar}{i}\frac{d}{dx}$ (take $\frac{d}{dx}$ and multiply $\frac{\hbar}{i}$) [this will be the momentum operator in QM]

$$\hat{A}\,\underbrace{\sin kx}_{f(x)} = \underbrace{\frac{\hbar k}{i}\cos kx}_{g(x)} \;;$$

$$\hat{A}\,\underbrace{e^{ikx}}_{f(x)} = \frac{\hbar}{i}\cdot ik\,e^{ikx} = \underbrace{\hbar k\,e^{ikx}}_{g(x)}$$

[Note relationship between g(x) and f(x) in this example, more about it later in Sec.E] e.g. $\hat{A} = \frac{d}{dx} x$ [this is not "1", take in $f(x)$, multiply it by x, then $\frac{d}{dx}$]

$$\hat{A} \underbrace{\cos kx}_{f(x)} = \frac{d}{dx}(x \cos kx) = \underbrace{\cos kx - kx \sin kx}_{g(x)}$$

e.g. $\hat{A} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx}\right)\left(\frac{\hbar}{i}\frac{d}{dx}\right)$ [this will be the operator representing the kinetic energy in QM]

$$\hat{A} \underbrace{(3x^4 + 2x^2)}_{f(x)} = \frac{-\hbar^2}{2m} \underbrace{(36x^2 + 4)}_{g(x)}$$

$$\hat{A} e^{ikx} = \frac{-\hbar^2}{2m}(ik)(ik) e^{ikx} = \frac{\hbar^2 k^2}{2m} e^{ikx}$$

$$\hat{A} \sin kx = \frac{\hbar^2 k^2}{2m} \sin kx$$

[Note relationship between g(x) and f(x) in these two cases, more about it later in Sec.E]

Here are two trivial but useful examples

e.g. $\hat{A} = a$ (just a constant, could be complex)

[take in $f(x)$ and multiply it by a]

$$\hat{A} f(x) = a f(x)$$

e.g. $\hat{A} = 1$ ("identity" operator, take $f(x)$ and multiply it by "1")

$$\hat{A} f(x) = f(x) \quad (\text{for all } f(x))$$

e.g. $\hat{A} = 0$ (take in $f(x)$ and multiply it by "0", thus returning 0)

$$\hat{A} f(x) = 0 \quad (\text{for all } f(x))$$

We have seen "differential operators". Operators can be in matrix form.

E.g. $\underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\hat{A}}$ [take in a column ( ) and return ( )]

$$\underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\hat{A}} \underbrace{\begin{pmatrix} 1 \\ 0 \end{pmatrix}}_{f} = \underbrace{\begin{pmatrix} 0 \\ 1 \end{pmatrix}}_{g} \quad ; \quad \underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\hat{A}} \underbrace{\begin{pmatrix} 1 \\ 1 \end{pmatrix}}_{f} = \underbrace{\begin{pmatrix} 1 \\ 1 \end{pmatrix}}_{g}$$

- So, operator is like a little program, taking in an input f and returning an output g

Let's extract some features of operators from these examples

C. Linear Operators: QM deals with Linear Operators

Definition

$$\hat{A}\left[c_1 f_1(x) + c_2 f_2(x)\right] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$$

defines linear operator $\hat{A}$

- Here, c_1 and c_2 are constants (could be complex constants)

$$\underbrace{\frac{\hbar}{i}\frac{d}{dx}}_{\hat{A}}\left[c_1 f_1(x) + c_2 f_2(x)\right] = c_1 \frac{\hbar}{i}\frac{d}{dx} f_1(x) + c_2 \frac{\hbar}{i}\frac{d}{dx} f_2(x) = c_1 \hat{A} f_1 + c_2 \hat{A} f_2$$

$\therefore$ $\boxed{\frac{\hbar}{i}\frac{d}{dx} \text{ is a linear operator}}$ (this will be the momentum operator)

Ex: How about $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$?

Ex: How about $\hat{A} = \text{SQRT}$?

How about $\hat{A} = x$? [take in $f(x)$ and multiply it by x]

$$\hat{A}[c_1 f_1 + c_2 f_2] = x[c_1 f_1 + c_2 f_2] = c_1 x f_1 + c_2 x f_2 = c_1 \hat{A} f_1 + c_2 \hat{A} f_2$$

$\therefore$ $\boxed{x \text{ is a linear operator}}$ (this will be the position operator)

Key Concepts

- Definition of linear operators
- $\frac{\hbar}{i}\frac{d}{dx}$ and x are linear operators

D. The ordering of two operators is a serious matter

- Operators $\hat{A}$ and $\hat{B}$

$$\hat{A}\hat{B}f(x) = \hat{A}\left(\hat{B}f(x)\right)$$

then $\hat{A}$ do $\hat{B}$ first

$$\hat{B}\hat{A}f(x) = \hat{B}\left(\hat{A}f(x)\right)$$

then $\hat{B}$ do $\hat{A}$ first

they may or may not give the same output

- Define Commutator of two operators $\hat{A}$ and $\hat{B}$

$$\hat{A}\hat{B} - \hat{B}\hat{A} \equiv [\hat{A}, \hat{B}]$$

Definition

so it is also an operator

Example: $\hat{A} = x$, $\hat{B} = \frac{\hbar}{i}\frac{d}{dx}$

[An important example]

$$[\hat{A}, \hat{B}]f(x) = \left[x, \frac{\hbar}{i}\frac{d}{dx}\right]f(x) = x\frac{\hbar}{i}\frac{d}{dx}f(x) - \frac{\hbar}{i}\frac{d}{dx}\big(xf(x)\big)$$

$$= \cancel{x\frac{\hbar}{i}\frac{d}{dx}f(x)} - \cancel{x\frac{\hbar}{i}\frac{d}{dx}f(x)} - \frac{\hbar}{i}f(x)$$

$$= i\hbar f(x)$$

$\therefore \left[x, \frac{\hbar}{i}\frac{d}{dx}\right]f(x) = i\hbar f(x)$ for <u>all</u> $f(x)$

[Note: The keyword here is "for **all** f(x)"]

- When $[\hat{A}, \hat{B}]f(x) = (\text{something})\, f(x)$ is true for <u>all</u> $f(x)$, we assign that (something) to the commutator

$\therefore \boxed{\left[x, \frac{\hbar}{i}\frac{d}{dx}\right] = i\hbar}$ [this is part of Dirac's 1933 Nobel Prize] for his 1925 work

When $[\hat{A}, \hat{B}] \neq 0$ (all $f(x)$), we say

Operators $\hat{A}$ and $\hat{B}$ do not commute

Thus $\boxed{x \text{ and } \frac{\hbar}{i}\frac{d}{dx} \text{ do not commute}}$

Example: $\hat{A} = \frac{\hbar}{i}\frac{d}{dx}$; $\hat{B} = -\hbar^2\frac{d^2}{dx^2}$

$$\left[\frac{\hbar}{i}\frac{d}{dx}, -\hbar^2\frac{d^2}{dx^2}\right]f(x) = -\frac{\hbar^3}{i}\frac{d^3}{dx^3}f(x) - \left(\frac{-\hbar^3}{i}\frac{d^3}{dx^3}f(x)\right) = 0 \quad \text{for } \underline{\underline{\text{all}}}\ f(x)$$

When $[\hat{A}, \hat{B}] = 0$ (all $f(x)$), operators $\hat{A}$ and $\hat{B}$ commute

Thus $\underbrace{\frac{\hbar}{i}\frac{d}{dx}}_{\text{momentum}}$ and $\underbrace{-\hbar^2\frac{d^2}{dx^2}}_{\text{momentum} \cdot \text{momentum}}$ commute

How about $\hat{A}\hat{A}f(x)$ [take in $f(x)$, do $\hat{A}f(x)$, take result and operate $\hat{A}$ again]

this is written as $\hat{A}^2 f(x)$, i.e. $\hat{A}^2 \equiv \hat{A}\hat{A}$, so $[\hat{A},\hat{A}]=0$

<u>Important to note</u>: $\hat{A}^2 f(x) \neq [\hat{A}f(x)]^2$ [Avoid common misconception]

e.g. $\hat{A} = \frac{\hbar}{i}\frac{d}{dx}$; $\hat{A}^2 = \hat{A}\hat{A} = \frac{\hbar}{i}\frac{d}{dx}\left(\frac{\hbar}{i}\frac{d}{dx}\right)$ (take in $f(x)$ and start from the right)

$$= -\hbar^2 \frac{d^2}{dx^2}$$

$\hat{A}^2 f(x) = -\hbar^2 \frac{d^2}{dx^2} f(x)$ ($\hat{A}^2$ is a <u>linear</u> operator)

But $[\hat{A}f(x)]^2 = \left[\frac{\hbar}{i}\frac{df(x)}{dx}\right]^2 = -\hbar^2\left[\frac{df(x)}{dx}\right]^2$ (not a linear operator)

In QM, we will encounter operators like $\hat{A}\hat{A} = \hat{A}^2$

Key Concepts

- Be very careful in handling two operators one after another
- $\hat{A}\,\hat{B}\,f(x)$ and $\hat{B}\hat{A}\,f(x)$ are generally not the same
- $[\hat{A}, \hat{B}] \equiv \hat{A}\,\hat{B} - \hat{B}\hat{A}$
- After checking on all $f(x)$,

  $[\hat{A}, \hat{B}] \neq 0$; $\hat{A}$ and $\hat{B}$ do not commute

  $[\hat{A}, \hat{B}] = 0$; $\hat{A}$ and $\hat{B}$ commute
- $[x, \frac{\hbar}{i}\frac{d}{dx}] = i\hbar$ is a fundamental commutator of QM
- Analogy : Rotating a book $\underbrace{\text{about } \hat{z}}_{\hat{A}}$ and $\underbrace{\text{about } \hat{x}}_{\hat{B}}$ by 90°

E. For an operator $\hat{A}$, there is a special set of functions called Eigenfunctions

In general, $\hat{A} f(x) = g(x)$

different and no simple relation between them

- Define the Eigenvalue Problem of an Operator $\hat{A}$

Look for functions $\phi(x)$ that satisfy

Definition

Eigenvalue problem →

$$\boxed{\hat{A}\, \underbrace{\phi(x)}_{\text{same function}} = \overset{\text{a constant (could be complex)}}{a}\, \underbrace{\phi(x)}_{\text{same function}}}$$

Names

- $\phi(x)$ is called an eigenfunction of $\hat{A}$ and the corresponding a is called its eigenvalue. "$\phi(x)$ and a" come in pair.

$$\hat{A}\,\phi(x) = a\,\phi(x)$$

- Stringent requirement! Guess any $f(x)$, usually NOT an eigenfunction[†]!
  $\therefore$ Need to solve the eigenvalue problem by math skills
- Solving $\hat{A}\,\phi(x) = a\,\phi(x)$
  - Not only solving for a, not only solving for $\phi(x)$
  - Solving for both $\phi(x)$ and a
  - Not only solving for one value of a and for one $\phi(x)$
  - Solving for many (all allowed) $\phi(x)$ and thus many a

$$\phi_1(x) \leftrightarrow a_1\ ;\quad \phi_2(x) \leftrightarrow a_2\ ;\quad \cdots,\ \phi_n(x) \leftrightarrow a_n\ ,\ \cdots$$

[†] In Chinese, eigenvalue is 本徵值 or 本征值, eigenfunction is 本徵(征)函數(数), eigenstate is 本徵(征)態

Go back to examples in Sec. B - Most examples give $g(x) \neq a f(x)$

But a few do show $\hat{A}\phi(x) = a\phi(x)$

$$\hat{A} = \frac{\hbar}{i}\frac{d}{dx} \quad ; \quad \hat{A}\underbrace{e^{ikx}}_{\text{eigenfunction}} = \underbrace{\hbar k}_{\text{eigenvalue}}\underbrace{e^{ikx}}_{\text{eigenfunction}}$$

Momentum operator in QM

How many of them?

True for any $k \Rightarrow$ infinitely many

Meaning:

$$\left.\begin{array}{l} e^{ik_1x} \leftrightarrow \hbar k_1 \\ e^{ik_2x} \leftrightarrow \hbar k_2 \\ \vdots \\ e^{ik_nx} \leftrightarrow \hbar k_n \\ \vdots \end{array}\right\}$$

All come out from one equation

$$\frac{\hbar}{i}\frac{d}{dx}\phi(x) = a\,\phi(x)$$

We have seen these functions before!

$\underbrace{e^{ikx}}$ Wave of definite k, thus definite λ, thus definite momentum

de Broglie

↳ state of definite momentum $p = \hbar k$

- Look at Math Structure (important idea here)

Momentum Operator in QM → $\frac{\hbar}{i}\frac{d}{dx} e^{ikx} = \underbrace{\hbar k}_{p} e^{ikx}$

The mathematical structure is:

Want to look for states of definite momenta and values of momenta?

Solve eigenvalue problem of the momentum operator!

Copying through (or guessing how Nature works at atomic scale)

How about...

Want to look for states of definite (some quantity) and values of (that quantity)?

Solve eigenvalue problem of (that quantity's) operator

The point is: *Nature really works this way!*

Therefore, eigenvalue problems are extremely important in QM

+ That (some quantity) could be, for example, total energy of a system, angular momentum, (angular momentum)^2, etc. How to write down $\hat{A}$ for each of these quantities?

Key concepts

- $\hat{A}\phi(x) = a\,\phi(x)$ defines an eigenvalue problem
- $\phi(x) \leftrightarrow a$ come in pair (they are to be solved)
- Typically, $\hat{A}\phi(x) = a\,\phi(x)$ is one equation for many $\phi(x)$'s and a's, i.e. $\phi_1(x) \leftrightarrow a_1$, $\phi_2(x) \leftrightarrow a_2$, ...
- Eigenvalue problems are a big part of Quantum Mechanics

This mathematical aside to operators and eigenvalue problems leads us back to a key remaining question in our discussion of quantum mechanics:

How to construct (or simply "write down") operators for various physical quantities? Is there a recipe?

Exercises (Do try them at home)

- Is $\begin{Bmatrix} \sin kx \\ \cos kx \end{Bmatrix}$ an eigenfunction of $\frac{\hbar}{i}\frac{d}{dx}$? If yes, what is the eigenvalue?

- Is $\left(\frac{\sqrt{Km}}{\hbar\pi}\right)^{1/4} e^{-\frac{\sqrt{Km}}{2\hbar}x^2}$ an eigenfunction of $\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}Kx^2\right)$?

  If yes, what is the eigenvalue? [m, K are constants]

[Hint: Plug in f(x), do the derivatives, check output g(x) and see if the definition of eigenfunction is satisfied]