X. More on Operators in QM

- In QM, physical quantities[+] are represented by <u>operators</u>
  - Construction: Think classical + Go Quantum $\underbrace{[x \to \hat{x},\ p_x \to \hat{p}_x,\ [\hat{x}, \hat{p}_x] = i\hbar]}$

    $\hat{x} \to x,\ \hat{p}_x \to \frac{\hbar}{i}\frac{\partial}{\partial x}$ is <u>a</u> way to go quantum
  - Saw: $\hat{x}$ (position), $\hat{p}_x$ (momentum)

    $\hat{T}$ (k.e.), $\hat{U}$ (p.e.)

    $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$, $\hat{L}^2$ (orbital angular momentum)
  - Eigenvalues of $\hat{A}$ are possible outcomes of measurements of A
  - Given $\hat{A}$ and a state Ψ, $\int \Psi^* \hat{A} \Psi \, d\tau \equiv \langle \hat{A} \rangle$ = expectation value

$\boxed{\text{Question: Do operators in QM take on a particular class?}}$

[+] Called dynamical variables usually

A. What's so special about QM Operators?

- Measurement outcomes
- Expectation values[+]

physical quantities — They must be **REAL**

$\therefore$ **Operator representing a physical quantity in QM must have real eigenvalues** — Key Point

Question becomes:

Which type of operators have real eigenvalues?

[+] E.g. We want to have $\int \Psi^* \hat{A} \Psi \, d\tau = \left[\int \Psi^* \hat{A} \Psi \, d\tau \right]^*$ for all Ψ (then $\langle A \rangle$ is real)

B. Hermitian Operators

$\boxed{\text{Hermitian Operators have real eigenvalues}}$ Key Point

- **What are they?**

• Ingredients in the definition: Operator $\hat{A}$, ANY $\overbrace{\text{well-behaved}}^{\text{vanishes at infinity}}$ functions $f(x)$ $[f(\vec{r})]$ and $g(x)$ $[g(\vec{r})]$ 1D [3D]

$\boxed{\text{Integral \#1}}$

$$\int f^* \hat{A}\, g\, d\tau = \underbrace{\int f^* \overbrace{(\hat{A} g)}^{\text{some function ①}} d\tau}_{\text{then inner product ②}}$$

$\boxed{\text{Integral \#2}}$

$$\underbrace{\int g \underbrace{(\hat{A} f)}_{①}{}^{*②}\, d\tau}_{③} = \underbrace{\int g \underbrace{\underbrace{\hat{A}^*}_{①} f^*}_{②}\, d\tau}_{③}$$

$\hat{A}^*$ = Complex conjugate of $\hat{A}$
[see "i", turn it into "$-i$"]

Integral #1 & Integral #2 are two different things in general.

Definition+

(1) If $\underbrace{\int f^* \hat{A} g \, d\tau}_{\#1} = \underbrace{\int g \hat{A}^* f^* d\tau}_{\#2} = \underbrace{\int (\hat{A} f)^* g \, d\tau}_{\#2}$ (for any f & g)

#2 ← same → #2

then $\hat{A}$ is a Hermitian Operator

In fancy notations: $\langle f | g \rangle \equiv \int f^* \cdot g \, d\tau$ [inner product]

(1) becomes $\langle f | \hat{A} g \rangle = \langle \hat{A} f | g \rangle$ for any f & g defines Hermitian Operator

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+1/. Must Stare at definition to get what the requirement on $\hat{A}$ is about for it to be Hermitian

2/. In some books, the definition relies on one (any) function: $\int f^* \hat{A} f \, d\tau = \int f \hat{A}^* f^* d\tau$. Here, we use a more ordinary one.

Remarks

- $\hat{A}^*$ (see "i" in $\hat{A}$, turn it into "$-i$")
- In this Chapter, we consider $\underbrace{\text{operators in QM}}_{\text{linear}}$ and $\underbrace{\text{functions in QM}}_{\text{well-behaved}}$,
- <u>Dirac Notation</u>

$$|g\rangle \rightarrow g(x) \quad ; \quad \langle f| \rightarrow f^*(x)$$

When "$\langle\ |$" meets "$|\ \rangle$", there is an integral (inner product)

$$\langle f|g\rangle = \int f^*(x)\, g(x)\, dx$$

$$\langle f|\hat{A}g\rangle \underset{\text{also written as}}{=} \langle f|\hat{A}|g\rangle = \int f^*(x)\, \hat{A}\, g(x)\, dx$$

$\{\psi_1, \psi_2, \ldots, \psi_n, \ldots\}$ orthonormal set of functions

$$\int \psi_n^*(x)\, \psi_m(x)\, dx = \delta_{nm} \iff \underbrace{\langle \psi_n | \psi_m \rangle = \delta_{nm}}_{\text{can simplify notation to}} \quad \text{Dirac Notation}$$

$$\langle n | m \rangle = \delta_{nm}$$

- We used "$d\tau$" in (1): could mean dx (1D), d^2r (or $dx\,dy$) (2D), or d^3r (or $dx\,dy\,dz$) (3D)

Question: Is $\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$ Hermitian?

$$\int_{-\infty}^{\infty} f^* \underbrace{\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)}_{\hat{A}} g\, dx = \frac{\hbar}{i} \cancel{f^* g \Big|_{-\infty}^{\infty}} - \int_{-\infty}^{\infty} g \frac{\hbar}{i}\frac{\partial}{\partial x} f^* dx \quad \text{[integration by parts]}$$

f, g vanish at infinity (well-behaved)

$$= \int_{-\infty}^{\infty} \underbrace{\left[\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^* f^*\right]}_{(\hat{A}^* f^*)} g\, dx = \int_{-\infty}^{\infty} g \left[\frac{\hbar}{i}\frac{\partial}{\partial x} f\right]^* dx$$

$\therefore$ $\hat{p}_x$ satisfies the definition. It is a Hermitian Operator.

Ex: Show that $\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ is Hermitian.

[Hint: Use "by parts" twice]

Is $\hat{x}$ Hermitian? ($\because$ just multiply 3 functions of x)

$$\int f^* x\, g\, dx = \int g\, x\, f^* dx = \int g \underbrace{x^*}_{=x} f^* dx$$

$\therefore$ $\hat{x} = x$ is Hermitian

By the same argument,† $U(x)$ is Hermitian.

$\hat{H} = \hat{T} + \hat{U}$ is also Hermitian

[$\because$ If $\hat{A}$, $\hat{B}$ are Hermitian, $\hat{C} = \hat{A} + \hat{B}$ is also Hermitian. (Ex.)]

Ex: Check that all the Operators listed in the table are Hermitian.

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† $U(\hat{x})$? What is a function of an operator?

A list of commonly used quantities: *Think Classical*, then *Go Quantum*

Carry this list with you

Classical-Mechanical Observables and Their Corresponding Quantum-Mechanical Operators

Observable		Operator	
Name	Symbol	Symbol	Operation
Position	x	$\hat{X}$	Multiply by x
	$\mathbf{r}$	$\hat{\mathbf{R}}$	Multiply by $\mathbf{r}$
Momentum	p_x	$\hat{P}_x$	$-i\hbar\frac{\partial}{\partial x}$
	$\mathbf{p}$	$\hat{\mathbf{P}}$	$-i\hbar(\mathbf{i}\frac{\partial}{\partial x}+\mathbf{j}\frac{\partial}{\partial y}+\mathbf{k}\frac{\partial}{\partial z})$
Kinetic energy	T_x	$\hat{T}_x$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
	T	$\hat{T}$	$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})$ $=-\frac{\hbar^2}{2m}\nabla^2$
Potential energy	$V(x)$	$\hat{V}(\hat{x})$	Multiply by $V(x)$
	$V(x, y, z)$	$\hat{V}(\hat{x}, \hat{y}, \hat{z})$	Multiply by $V(x, y, z)$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})$ $+V(x, y, z)$ $=-\frac{\hbar^2}{2m}\nabla^2+V(x, y, z)$
Angular momentum	$l_x = yp_z - zp_y$	$\hat{l}_x$	$-i\hbar(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y})$
	$l_y = zp_x - xp_z$	$\hat{l}_y$	$-i\hbar(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z})$
	$l_z = xp_y - yp_x$	$\hat{l}_z$	$-i\hbar(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x})$

List taken from McQuarrie's *Quantum Chemistry*

(a) Hermitian Operators give real expectation Value

From Eq.(1) [definition], take $f = g = \Psi$ ← state for getting expectation value

$$\int \Psi^* \hat{A} \Psi \, d\tau = \langle \hat{A} \rangle = \int (\hat{A}\Psi)^* \Psi \, d\tau \quad [\because \hat{A} \text{ is Hermitian}]$$

$$= \int \Psi (\hat{A}\Psi)^* \, d\tau \quad [\text{order doesn't matter in multiplying two functions}]$$

$$= \left[\int \Psi^* \hat{A} \Psi \, d\tau \right]^*$$

$$= \langle \hat{A} \rangle^* \qquad (\text{True for } \underline{\text{any}}^{\dagger}\ \Psi)$$

$\Rightarrow \langle \hat{A} \rangle$ is Real (as required by physics consideration)

$\therefore$ Hermitian Operator gives real expectation value, regardless of the state.

<u>Remark</u>: A "reverse" statement can be proven, i.e. an operator that gives real expectation value must be a Hermitian operator. The proof is beyond the scope of our course.

† Of course, Ψ should be well-behaved as required by physics.

(b) Hermitian Operators have real eigenvalues

Let $\hat{A}$ be a Hermitian Operator

$$\hat{A}\phi_n = a_n \phi_n \quad \text{(i) [eigenvalue problem of } \hat{A}\text{] } (\underline{a_n \text{ are eigenvalues}})$$

then $$\hat{A}^* \phi_n^* = a_n^* \phi_n^* \quad \text{(ii) [take complex conjugate of eigenvalue problem]}$$

From (i): $$\int \phi_n^* \hat{A} \phi_n \, d\tau = a_n \int \phi_n^* \phi_n \, d\tau \quad [\underbrace{a_n \text{ eigenvalue}}_{\text{a number}} \text{, is } \underline{\text{not}} \text{ a function}]$$

From (ii): $$\int \phi_n \hat{A}^* \phi_n^* \, d\tau = a_n^* \int \phi_n \phi_n^* \, d\tau$$

$\hat{A}$ is Hermitian $\Rightarrow$ $$\int \phi_n^* \hat{A} \phi_n \, d\tau = \int \phi_n \hat{A}^* \phi_n^* \, d\tau \quad (\text{so (i)} = \text{(ii)})$$

$$\therefore \quad a_n \int |\phi_n|^2 d\tau = a_n^* \int |\phi_n|^2 d\tau \Rightarrow \underbrace{a_n = a_n^*}$$

This is the most important property of Hermitian Operators. $\quad \therefore \boxed{a_n \text{ is real}}$ true for all eigenvalues

(C) <u>Eigenstates corresponding to different eigenvalues are orthogonal</u>

- This statement is about two <u>non-degenerate</u> states

$$\hat{A}\psi_n = a_n\psi_n \;\; \text{(i)} \; ; \quad \hat{A}\psi_m = a_m\psi_m \;\; \text{(ii)} \quad (\underbrace{a_n \neq a_m}_{\text{different eigenvalues}})$$

From (ii): $\hat{A}^*\psi_m^* = a_m\psi_m^*$ ($\because$ a_m is real, $\hat{A}$ is Hermitian)

$$\left.\begin{aligned} \int \psi_n \hat{A}^* \psi_m^* \, d\tau &= a_m \int \psi_n \psi_m^* \, d\tau \\ \overset{\hat{A}\text{ is Hermitian}}{\|} \qquad & \qquad\qquad \| \\ \int \psi_m^* \hat{A} \psi_n \, d\tau &= a_n \int \psi_m^* \psi_n \, d\tau \end{aligned}\right\} \Rightarrow (a_m - a_n)\int \psi_m^* \psi_n \, d\tau = 0$$

$$\Rightarrow \boxed{\int \psi_m^* \psi_n \, d\tau = 0} \quad \because a_m \neq a_n$$

This is exactly what we saw in 1D Box, 1D Harmonic Oscillator, 1D finite well, ..., as $\hat{H}$ in these problems are Hermitian.

- How about $\underbrace{\psi_{n1} \text{ and } \psi_{n2}}_{\text{degenerate state?}}$ with the <u>same</u> a_n?

Key Point → | No problem! One can <u>always</u> <u>make</u> degenerate states <u>orthogonal</u> to each other |
|---|

<u>E.g.</u> $\psi_{n1}, \psi_{n2} \leftrightarrow a_n$ (but ψ_{n1}, ψ_{n2} not orthogonal)

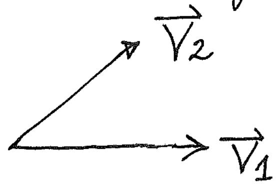
- Construct $\psi'_{n2} = \left[\int \psi^*_{n1} \psi_{n2} \, d\tau\right] \psi_{n1} - \psi_{n2}$ (see <u>picture</u> for idea)

(i) $\psi'_{n2} \leftrightarrow a_n$, (ii) ψ'_{n2} and ψ_{n1} are orthogonal

check $\int \psi^*_{n1} \psi'_{n2} \, d\tau = \left[\int \psi^*_{n1} \psi_{n2} \, d\tau\right] \cdot \underline{1} - \int \psi^*_{n1} \psi_{n2} \, d\tau = 0$

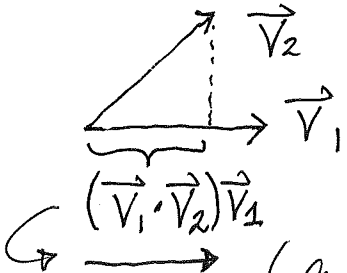
$\therefore$ $\underbrace{\psi_{n1} \text{ and } \psi'_{n2}}_{\text{both corresponding to eigenvalue } a_n}$ are orthogonal (still degenerate), even ψ_{n1}, ψ_{n2} are not.

- Easier to <u>visualize</u> construction using vectors



$\vec{V}_1$ and $\vec{V}_2$ are not orthogonal (they are unit vectors)
(<u>Analogy</u>: ψ_{n1} and ψ_{n2} are not orthogonal)

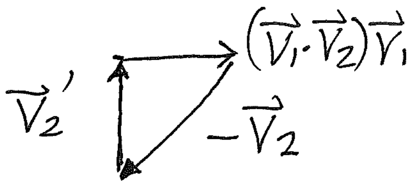
- Project $\vec{V}_2$ onto $\vec{V}_1$



(a properly scaled vector, shorter than $\vec{V}_1$)

<u>analogous</u> to $\left[\int \psi_{n1}^* \psi_{n2} \, d\tau\right] \psi_{n1}$

- Form $\vec{V}_2{}' = (\vec{V}_1 \cdot \vec{V}_2)\vec{V}_1 - \vec{V}_2$



$\therefore \ \vec{V}_2{}' \perp \vec{V}_1$

[then one can normalize $\vec{V}_2{}'$]

<u>analogous</u> to forming

$$\psi_{n2}' = \left[\int \psi_{n1}^* \psi_{n2} \, d\tau\right] \psi_{n1} - \psi_{n2}$$

ψ_{n2}' and ψ_{n1} are orthogonal by construction

[then one can normalize ψ_{n2}']

C. Measurements

- Now, we can back up what we stated earlier about measurement theory
- Measurement : Needs a Quantity $\hat{A}$
  and a state (before measurement) ψ

$$\hat{A}\,\phi_n = a_n\,\phi_n \quad [\text{eigenvalue problem of } \hat{A}]$$

$\{\phi_n\}$ are orthonormal, a_n's are real ($\because$ $\hat{A}$ is $\underbrace{\text{Hermitian}}_{}$) QM operators

Expand $\psi = \sum_n c_n \phi_n$ can always be done

and $\underbrace{c_n = \int \phi_n^* \psi \, d\tau}_{\text{used } \{\phi_n\} \text{ are orthonormal}} \Rightarrow c_n$ are known for given ψ

Evaluate expectation value $\langle \hat{A} \rangle$

$$\underbrace{\langle \hat{A} \rangle}_{\text{Mean } A} = \int \psi^* \hat{A} \psi \, d\tau = \int \left(\sum_m c_m^* \phi_n^* \right) \hat{A} \left(\sum_n c_n \phi_n \right) d\tau$$

$$= \sum_m \sum_n c_m^* c_n \int \phi_n^* \underline{\hat{A} \phi_n} \, d\tau$$

$$= \sum_m \sum_n c_m^* c_n a_n \int \phi_m^* \phi_n \, d\tau \quad [\because \hat{A}\phi_n = a_n \phi_n]$$

$$= \sum_m \sum_n c_m^* c_n a_n \delta_{mn}$$

$$= \sum_n |c_n|^2 a_n$$

$$= \underbrace{|c_1|^2}_{\substack{\text{prob. of} \\ \text{getting } a_1}} a_1 + \underbrace{|c_2|^2}_{\substack{\text{prob. of} \\ \text{getting } a_2}} a_2 + \cdots + \underbrace{|c_n|^2}_{\substack{\text{prob. of} \\ \text{getting } a_n}} a_n + \cdots$$

$\therefore |c_n|^2 =$ Prob. of getting eigenvalue a_n when measuring $\hat{A}$ on the state ψ

Aside: Dirac Notation (for expressions on X-15)

$|\psi\rangle = \sum_n c_n |\phi_n\rangle$ OR $|\psi\rangle = \sum_n c_n |n\rangle$ (for $\psi = \sum_n c_n \phi_n$)

$c_n = \langle \phi_n | \psi \rangle$ OR $c_n = \langle n | \psi \rangle$ (for $c_n = \int \phi_n^* \psi \, d\tau$)

$\therefore |\psi\rangle = \sum_n \langle \phi_n | \psi \rangle |\phi_n\rangle$ OR $|\psi\rangle = \sum_n \langle n|\psi\rangle |n\rangle$

$= \sum_n |\phi_n\rangle\langle\phi_n|\psi\rangle$ OR $|\psi\rangle = \sum_n |n\rangle\langle n|\psi\rangle$

$= \underbrace{\left(\sum_n |\phi_n\rangle\langle\phi_n|\right)}\,|\psi\rangle$ OR $|\psi\rangle = \underbrace{\left(\sum_n |n\rangle\langle n|\right)}\,|\psi\rangle$

an operator that operates on $|\psi\rangle$ to give $|\psi\rangle$

$\Rightarrow \sum_n |\phi_n\rangle\langle\phi_n| = \hat{1}$ ← identity operator OR $\sum_n |n\rangle\langle n| = \hat{1}$

a statement of $\{\phi_1, \phi_2, \ldots \phi_n, \ldots\}$ being a complete set

- Given that $\{\phi_1, \phi_2, \ldots, \phi_n, \ldots\}$ (e.g. all energy eigenstates) play the role of basis vectors in expanding any state ψ; the mathematical structure+ of QM is that of the high-dimensional (infinite dimension if $\{\phi_n\}$ has infinite members) linear vector space.

Note: Not to confuse with the dimension of the physical problem

e.g. 1D harmonic oscillator / Box
- physical problem is 1D
- Math structure is infinite dimension

+ This remark can be skipped if it is too abstract for you. We don't need it here.

Remark 1: Hermitian Matrix

$\hat{A}$ is Hermitian $\Rightarrow$ $\int f^* \hat{A}\, g\, dx = \left[\int g^* (\hat{A} f)\, dx\right]^* = \int (\hat{A} f)^* g\, dx$

any f and g

Instead of f & g, use notations $\{f_1, f_2, \cdots, f_i, \cdots\}$ for arbitrary functions

$$\underbrace{\int f_i^* \hat{A} f_j\, dx}_{\text{two indices}} = \underbrace{\left[\int f_j^* \hat{A} f_i\, dx\right]^*}_{\text{this is then } A_{ji}^*} \quad \text{defines Hermitian } \hat{A}$$

two indices

like a matrix element

call it A_{ij}

this is then A_{ji}^*

$\hat{A}$ has the property, when represented by matix elements, $A_{ij} = A_{ji}^*$

$$\begin{pmatrix} 1 & i & 1+2i \\ -i & 2 & 4 \\ 1-2i & 4 & 3 \end{pmatrix}$$ is a Hermitian Matrix

Diagonal elements: Real ($\because A_{ii}^* = A_{ii}$)

$A_{12} = i$, $A_{21} = -i$ $\Rightarrow$ $A_{12}^* = (i)^* = -i = A_{21}$

QM is $\left\{ \begin{array}{l} \text{full of Hermitian Operators} \\ \text{full of } \underbrace{\text{Hermitian Matrices}}_{\substack{\text{real eigenvalues} \\ \text{orthogonal eigenvectors}}} \end{array} \right.$

closely related (see perturbation chapter)

Remark 2: Hermitian Conjugate of an operator

- For our purposes, the definition [(1) on p. X-4] of Hermitian operator is sufficient
- In reading books, we may encounter related (but different) idea of $\underbrace{\text{Hermitian conjugate of an operator } \hat{A}}$

it is about another operator which is called the Hermitian conjugate of the operator $\hat{A}$

$\underbrace{\text{Given } \hat{A}}$, let $\hat{a}$ (another operator "baby $\hat{A}$") be the Hermitian conjugate

Evaluate $\int f^* \hat{A}\, g\, dx$ for any f and g

What is $\hat{a}$? Find $\hat{a}$ such that

$$\int (\hat{a} f)^* g \, dx \underset{\text{defines } \hat{a}}{=} \int f^* \hat{A} g \, dx \qquad (R1)$$

<u>Notation:</u> Instead of $\hat{a}$, the symbol $\hat{A}^+$ is used for Hermitian Conjugate

$$\therefore \int (\hat{A}^+ f)^* g \, dx \underset{\text{defines } \hat{A}^+}{=} \int f^* \hat{A} g \, dx \qquad (R2)$$

<u>What is a Hermitian Operator then?</u>

$$\hat{A} \text{ is Hermitian} \Rightarrow \int f^* \hat{A} g \, dx = \int (\hat{A} f)^* g \, dx \qquad (1)$$

$\therefore$ $\boxed{\hat{A} \text{ is Hemitian if } \hat{A}^+ = \hat{A}}$ it is its own Hermitian Conjugate.