Back to Essential Quantum Mechanics

- How to construct operators for other physical quantities?
- Measurement of a quantity is related to the eigenvalue problem of that quantity and the measurement postulates

H. Why do we focus on $\hat{x}$ and $\hat{p}$? How about other physical quantities?

So far, $\hat{x} \to x$; $\hat{p}_x \to \frac{\hbar}{i}\frac{d}{dx}$ (similarly for $\hat{y}, \hat{p}_y$; $\hat{z}, \hat{p}_z$)

then $\hat{H}$ follows and TDSE/TISE follow

How about operators for other physical (mechanical) quantities?

- Hamiltonian Mechanics $H(x, p)$ [or $H(q, p)$ or $H(\{q_i, p_i\})$] governs the dynamics. Thus, x & p dominate the formulation.
- Other quantities?
  - Can be expressed in terms of x and p [or $\vec{x}$ and $\vec{p}$] [or $\{q_i, p_i\}$]

Recipe of writing operators for other quantities [c.f. recipe of writing $\hat{H}$]

Step 1 : Think classical

Write down the quantity as it is in classical mechanics in terms of position and momentum [generalized coordinates/ momenta]

e.g. Kinetic energy $T = \frac{p^2}{2m}$ (1D)

Step 2 : Go Quantum

Substitute $x \to \hat{x} \to x$ and $p \to \hat{p} \to \frac{\hbar}{i}\frac{d}{dx}$ into classical expression

$\Rightarrow$ Quantum Operator of the quantity

e.g. Kinetic energy operator $\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ (Done!)

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*

Example: Angular Momentum Operator

<u>Step 1</u>: <u>Think Classical</u>

position (appears 1st)

momentum (appears 2nd)

$$\vec{L} = \vec{r} \times \vec{p}$$

vector (3 components) "cross product"

or in components $\vec{r} = (x, y, z)$; $\vec{p} = (p_x, p_y, p_z)$

$$L_x = y p_z - z p_y \; ; \; L_y = z p_x - x p_z \; ; \; L_z = x p_y - y p_x$$

<u>Step 2</u>: <u>Go Quantum</u>

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

Done!

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Extension (Ex.)

- What are $[\hat{L}_x, \hat{L}_y]$, $[\hat{L}_y, \hat{L}_z]$, $[\hat{L}_z, \hat{L}_x]$?

- There is a quantity $L^2 = L_x^2 + L_y^2 + L_z^2$ for the $(\text{magnitude})^2$ of $\vec{L}$,
  What is $\hat{L}^2$?

- What are $[\hat{L}^2, \hat{L}_x]$, $[\hat{L}^2, \hat{L}_y]$, $[\hat{L}^2, \hat{L}_z]$?

Do try these at home! All you need to know is the commutator [x,p]

Remark: Angular Momentum is a big business in QM. We will do more about it later.

Example: Interaction energy of an electric dipole moment due to a charge with an Electric field $\vec{E} = \vec{\mathcal{E}}_0 \cos\omega t = \mathcal{E}_0 \hat{k} \cos\omega t$ (in z-direction)

Step 1: Think Classical

charge q at position $\vec{r}$ from origin

$$\vec{\mu}_e = \text{electric dipole moment} = q\vec{r}$$

$$H' \equiv \text{Interaction energy} = \underbrace{-\vec{\mu}_e \cdot \vec{\mathcal{E}}}_{\text{classical EM}} = -q\,\mathcal{E}_0 \underbrace{\vec{r}\cdot\hat{k}}_{\substack{\text{picks up} \\ z\text{-component} \\ \text{of } \vec{r}}} \cos\omega t = -q\,\mathcal{E}_0 \underset{\substack{\uparrow \\ z\text{-component of position} \\ \text{of charge } q}}{z} \cos\omega t$$

Step 2: Go Quantum

$$\hat{H}' = -q\,\mathcal{E}_0 \underset{\substack{\uparrow \\ \text{operator}}}{\hat{z}} \cos\omega t$$

Done! (There is time t in it)

This is important for studying atoms interacting with light

Key Concepts

- With $\hat{x}$ and $\hat{p}_x$ [etc.], other operators can be constructed
- Recipe: "Think Classical" then "Go Quantum"
- See list of commonly used quantities and their QM operators
- An observation: All operators of physical quantities (often called observables) are Linear Operators

Next question: OK! Every classical mechanical observable is represented by a corresponding quantum mechanical operator, ***so what***?

I. Eigenvalues of $\hat{A}$ represent the possible results of carrying out a measurement of the value of the quantity A

- This is a postulate of QM (one that deals with measurements)
- Important idea: Generally speaking, we need two pieces of information in considering measurements
  - Physical quantity to be measured $A \rightarrow \hat{A}$ (operator)
  - The state (wavefunction) of the system $\Psi(\vec{r},t)$ on which measurement of A is to be done

[E.g. Hydrogen atom only specifies the *system*, measuring the position of the electron specifies the quantity A to be measured, but still need the state of the hydrogen atom Ψ(x,t) (describing the electron) on which measurement is to be made.]

[Note: This section is a bit abstract. Don't worry. Things will become clearer when you see more examples.]

- <u>Statement on result</u> when there is <u>no additional information</u> on $\Psi(\vec{r},t)$

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

Recall:

$$\underbrace{\begin{matrix}\phi_1(x)\\ \phi_2(x)\\ \vdots\\ \phi_n(x)\\ \vdots\end{matrix}}_{\text{eigenfunctions of }\hat{A}} \begin{matrix}\leftrightarrow\\ \leftrightarrow\\ \\ \leftrightarrow\\ \\ \end{matrix} \underbrace{\begin{matrix}a_1\\ a_2\\ \vdots\\ a_n\\ \vdots\end{matrix}}_{\text{eigenvalues of }\hat{A}}$$

Postulate says:
Outcome of a measurement must be <u>an eigenvalue</u> of $\hat{A}$

This is as much as QM can say about outcome of a measurement with <u>no information</u> on $\Psi(\vec{r},t)$

Follow-up questions

Which eigenvalues will show up as measurement result?

General answer: Don't know if no information on $\Psi(\vec{r},t)$

Better answer: Tell me more about the state $\Psi(\vec{r},t)$

[e.g. if $\Psi(\vec{r},t) = \phi_{13}(x)$, then 100% sure a_{13} will show up.
But it is a very special case] (more later)

Can we tell which eigenvalue will show up with what probability?

General answer: No if there is no information on $\Psi(\vec{r},t)$

Better answer: Tell me $\Psi(\vec{r},t)$ and we can work it out

[e.g. if $\Psi = c_1\phi_1 + c_{13}\phi_{13}$, then a_1 shows up with Prob. $|c_1|^2$
a_{13} shows up with Prob. $|c_{13}|^2$]

And other eigenvalues has no chance to show up

A related Postulate about what happens ***Immediately after*** a measurement

- Measurement on A : $\{a_1, a_2, \cdots, a_n, \cdots\}$

  one eigenvalue will show up (statement on outcome <u>before</u> measurement)

  Let's say result of measurement is a_i (the i^{th} eigenvalue)

Postulate says : <u>Immediately</u> after the measurement,
[at no time after measurement]
the <u>wavefunction</u> of the system <u>becomes</u> the <u>eigenfunction</u> ϕ_i
corresponding to the measurement result a_i

Pictorially,

$$\Psi(\vec{r},t) \xrightarrow[\text{Immediate after measurement}]{\text{Measurement of } A \text{ gives } a_i} \phi_i$$

Before Measurement

right after measurement

This is what is called the ***Collapse of wavefunction*** after a measurement. The outcome (result) of a measurement determines the wavefunction ***right after*** the measurement.

Why do we stress "***immediately after* a measurement**"?

What if we made a measurement before lunch and look at the wavefunction after lunch?

Immediately after measurement (before lunch) $\Psi(x, t_0) = \phi_i(x, t_0)$

before lunch

$\xrightarrow{\text{lunch time}}$ What is $\Psi(x, t)$?

after lunch

Different from right after measurement

[Initial Value Problem] (discussed) [using TDSE]

Implicit in this postulate of wavefunction collapse is a *reasonable expectation* of…

> If the state before measurement of A is an eigenfunction $\phi_i(x)$ of $\hat{A}$, then the measurement result is 100% certain to be a_i

"Reasoning" for collapsing to $\phi_i(x)$ immediately after measurement

- Measurement gives one of the eigenvalues
- Measurement result is a_i (wavefunction changed to something)
- Immediately after getting a_i, do a second measurement of A, believe the result should be a_i again. (It is a reasonable expectation)
- Thus, wavefunction must be $\phi_i(x)$ before the 2nd measurement
- Hence, wavefunction after 1st measurement (same as before 2nd measurement) must be $\phi_i(x)$, once the result a_i is obtained

[Remark: In Ch.I, we discussed 1-slit and 2-slit experiments using electrons and their implications. The discussion here on operator and measurement is just stating the same points in Ch.I but in a slightly mathematical and abstract way. Again, things will be clearer after you see some examples.]

Key Concepts (Postulates)

- Classical mechanical quantities $\rightarrow$ QM operators
- $\hat{A}\,\phi(x) = a\,\phi(x)$ [eigenvalue problem] is important
- Measurement: Measuring what (A, thus $\hat{A}$) and on what state ($\Psi(\vec{r},t)$)
- Measurement of A: result must be one of the eigenvalues $\{a_1, a_2, \cdots, a_n, \cdots\}$
- Immediately after measurement that gives a_i, wavefunction becomes eigenfunction $\phi_i(x)$ corresponding to a_i

These statements, so far, do not need information on $\Psi(\vec{r},t)$

This ends Chapter IV in which we developed some essential concepts about mathematical operators and the operators that we will encounter in quantum mechanics.

QM operators can be constructed systematically from classical mechanics plus the position and momentum operators.

Eigenvalue problems are an important part of QM. TISE is an eigenvalue problem.

Measurement is a big business in QM.

Result of a measurement is related to the eigenvalue problem of what is being measured.

The following *Intermission Chapter* summarizes what we have so far.

We will start doing quantum mechanical calculations.