Probability Theory

[DISCRETE CASE]

Consider a physical measurement of a variable $V$ which gives discrete set of outcomes $\{V_i, i \in I\}$

$I$ = set of integers. Let $N$ be the total number of measurements. Let $N_i$ measurements yield a value $V_i$.

$$N = \sum_{i \in I} N_i$$

The probability of finding a value $V_i$ is given by

$$P(V_i) = \frac{N_i}{N}$$

The most probable value of $V$ is one for which $N_i$ is the largest of all possible $N_i$. Its probability is

$$P_{mp}(V_i) = \text{maximum } \{N_i, i \in I\}$$

The average value of $V$ denoted by $<V>$ is also known as its expectation value. It is defined as

$$<V> = \sum_{i \in I} V_i P(V_i) = \frac{\sum_{i \in I} V_i N_i}{N}$$
The variance ($\sigma^2$) of $V$ is defined by

$$\sigma^2 \equiv \langle (V - \langle V \rangle)^2 \rangle,$$ (Note $\sigma^2 \geq 0$ always)

$$\therefore \sigma^2 = \langle V^2 + \langle V \rangle^2 - 2V\langle V \rangle \rangle$$ \[3-2\]

Note that, if $f(V)$ is a function of $V$ then

$$\langle f(V) \rangle \equiv \sum_{i \in I} f(V_i)P(V_i)$$

$$\therefore \sigma^2 = \sum_{i \in I} V_i^2P(V_i) + \sum_{i \in I} \langle V \rangle^2P(V_i)$$

$$- 2 \sum_{i \in I} V_i\langle V \rangle P(V_i)$$

Note $\langle V \rangle$ and hence $\langle V \rangle^2$ do not depend on $i$. Also

$$\sum_{i \in I} P(V_i) = 1, \therefore \sum_{i \in I} N_i = N,$$

$$\therefore \sigma^2 = \langle V^2 \rangle + \langle V \rangle^2 - 2\langle V \rangle^2$$

$$= \langle V^2 \rangle - \langle V \rangle^2$$

The standard deviation ($\sigma$) is defined by

$$\sigma \equiv \sqrt{\langle (V - \langle V \rangle)^2 \rangle} \equiv \sqrt{\sigma^2}$$
Note also that $\sigma^2 = \frac{1}{10}$

$\Rightarrow \frac{\sigma^2}{7} \geq \frac{\sigma^2}{7^2}$

[CONTINUUM CASE]

If $V$ is a continuous variable and measurement of $V$ can give any real value, i.e., $V \in \mathbb{R}$, then the probability $P(V_o)$ of finding any fixed and exact value $V_o$

$P(V_o) = 0$, $\forall v_o \in \mathbb{R}$.

However, if we define $P(V_o)$ as the probability of finding a value of $V$ between $V_o$ and $V_o + dV$ then

$P(V_o) = p(v_o) dV$, $V_o \in \mathbb{R}$

where $p(V)$ is called the probability density of $V$. Note that

$$\int_{\mathbb{R}} p(V) dV = 1$$

$\Rightarrow p(V)$ has dimensions of $1/V$.

Probability of $V$ being in an interval $[V_1, V_2]$, $V_2 > V_1$, is
\[ P(v \in [v_1, v_2]) = \int_{v_1}^{v_2} p(v) \, dv \]

Also \[ \langle f(v) \rangle = \int_{v\in \mathbb{R}} f(v) p(v) \, dv \]

\[ \sigma^2 = \int_{v\in \mathbb{R}} (v - \langle v \rangle)^2 p(v) \, dv \]

\[ = \langle v^2 \rangle - \langle v \rangle^2 \]

\[ = \int_{v\in \mathbb{R}} v^2 p(v) \, dv - \left[ \int_{v\in \mathbb{R}} v p(v) \, dv \right]^2 \]

\[ \sigma = \sqrt{\sigma^2} \]

Most probable value happens when \( p(v) \) is maximum

\[ \frac{dp(v)}{dv} \bigg|_{v=v_m} = 0 \quad \text{and} \]

\[ \frac{d^2 p}{dv^2} \bigg|_{v=v_m} < 0 \]
Postulates of Quantum Mechanics (QM).

We state below the postulates of non-relativistic QM along with their analogs in Classical Mechanics (CM). For simplicity we will initially consider only one space dimension and QM of only one particle.

CM

| The state of a particle at time \( t \) is defined by its position \( x(t) \) and momentum \( p(t) = m \frac{dx(t)}{dt} \), i.e. as a point in phase space \((x(t), p(t))\). |

| Every dynamical variable \( w \) is a function of \( x \) and \( p \), i.e. \( w = w(x, p) \). Example: kinetic energy \( T = \frac{1}{2}mv^2 = \frac{p^2}{2m} \). |

QM

| The state of a particle is defined by a wavefunction \( \psi(x, t) \) in Hilbert space (HS). HS is the space of all square-integrable functions, \( f(x) \in \mathbb{R}, \int_{-\infty}^{\infty} |f(x)|^2 \, dx \in \mathbb{R} \). |

| The independent variables \( x \) and \( p \) of CM are represented by operators \( \hat{X} \) and \( \hat{P} \). They have forms \( \hat{X} = x \) and \( \hat{P} = -i\hbar \frac{d}{dx} \). The operators \( \hat{\Sigma}(\hat{X}, \hat{P}) \) corresponding to classical... |
If the particle is in a state given by \( (x(t), p(t)) \) the measurement of the variable \( \omega(x, p) \) will yield a value \( \omega \). The state will remain unaffected.

Let the state of the particle be given by \( \Psi(x, t) \). Let \( \hat{D} \) be an operator with discrete eigen-values \( \omega_n \) and eigen-functions \( \phi_n(x) \) so that

\[
\Psi(x, t) = \sum_n c_n(t) \phi_n(x)
\]

and

\[
\hat{D} \phi_n(x) = \omega_n \phi_n(x)
\]

Then the measurement of the variable corresponding to \( \hat{D} \) will yield one of the eigen-values \( \omega_n \) with probability \( P(\omega_n) \)

\[
P(\omega_n) \propto |c_n(t)|^2
\]

If \( \Psi(x, t) \) is normalized, i.e., \( \int |\Psi(x, t)|^2 dx = 1 \), then

\[
P(\omega_n) = |c_n(t)|^2
\]
For an operator $\hat{N}_c$ with a continuous eigen-spectrum $\beta$ we get

\[ \Psi(x, t) = \int_{-\infty}^{\infty} c(\beta, t) \phi_\beta(x) \, d\beta \]

\[ \hat{N}_c \phi_\beta(x) = \beta \phi_\beta(x) \]

\[ P(\beta) \propto |c(\beta, t)|^2 \]

If $\Psi(x, t)$ is normalized

\[ P(\beta) = |c(\beta, t)|^2 \]

As a result of the measurement of $\hat{N}_D$ the state of the system will change to $\phi_n(x)$ from $\Psi(x)$.

For measurement of $\hat{N}_c$ it will change to $\phi_\beta(x)$ from $\Psi(x)$.

This is called the "Measurement" or "Collapse" Postulate of P.M.

The state variables change with time $t$ according to Hamilton's equations.

The wavefunction $\Psi(x, t)$ obeys the Schrödinger equation (TDSE)

\[ i \hbar \frac{\partial \Psi(x, t)}{\partial t} = \hat{H} \Psi(x, t) \]
\[ \dot{x} = \frac{\partial H_c(x, p)}{\partial p} \] and
\[ \dot{p} = -\frac{\partial H_c(x, p)}{\partial x} \]

where \( \hat{A} = \hat{A}(\hat{x}, \hat{p}) = H_c(x \rightarrow \hat{x}, p \rightarrow \hat{p}) \)
i.e. to obtain the quantum Hamiltonian operator \( \hat{H} \)
replace all classical variables like \( x \) and \( p \) by their corresponding quantum operators \( \hat{x} \) and \( \hat{p} \).

If
\[ H_c = \frac{\hat{p}^2}{2m} + V(x) \]
then
\[ \hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}) \]
\[ = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x). \]

TDSE = time dependent Schrödinger equation.

\[ \hbar = \text{Planck's constant} \]
\[ \hbar \equiv \frac{\hbar}{(2\pi)} \]
\[ \hbar = 6.63 \times 10^{-34} \text{ Joule second} \]
\[ = 6.63 \times 10^{-34} \text{ kg} \cdot \text{m}^2 / \text{s} \]

\([\hbar] = [M^1 L^2 T^{-2} ]\)
The inner product of two functions $f(x)$ and $g(x)$ is defined as

$$<f|g> = \int_a^b f^*(x)g(x)\,dx \text{ over the interval } [a, b].$$

Note $<f|g>^* = <g|f>.$

An operator $\hat{\phi}$ is defined to be Hermitian iff

$$<f|\hat{\phi}g> = <\hat{\phi}f|g>, \quad \forall f, g$$

i.e.

$$\int_a^b f^*(x)\hat{\phi}f(x)\,dx = \int_a^b [\hat{\phi}f(x)]^*f(x)\,dx$$

In most cases note that we will use $a=-\infty, b=\infty.$

It can be easily proved that eigenvalues of Hermitian operators are real. Let $f_q(x)$ be an eigenfunction of the operator $\hat{\phi}$ with eigenvalue $q.$

$$\Rightarrow \hat{\phi}f_q(x) = qf_q(x)$$

$\hat{\phi}$ is Hermitian $\Rightarrow q^* = q \Rightarrow q \in \mathbb{R}.$

Eigenvalues of a Hermitian operator are therefore always real.
Two functions are said to be orthogonal if their inner product is zero.

\[ \langle f | g \rangle = \langle g | f \rangle = 0. \]

For any operator \( \hat{Q} \) eigenfunctions with distinct eigenvalues \( q \) and \( q' \) (i.e., \( q \neq q' \)) are orthogonal, provided the spectrum of \( q \)'s is discrete.

Proof: Let \( \hat{Q} f_q(x) = q f(x) \)

Let \( \hat{Q} g_q'(x) = q' g(x) \)

\( \hat{Q} \) is Hermitian \( \Rightarrow \langle f | \hat{Q} g' \rangle = \langle \hat{Q} f | g' \rangle \)

\( q' \langle f | g \rangle = q^* \langle f | g \rangle \)

\( q', q \in \mathbb{R} \Rightarrow q^* = q \)

Also \( q' \neq q \Rightarrow \langle f | g \rangle = 0 \).

The eigenfunctions of an observable (Hermitian) operator are complete. I.e. any function in Hilbert space can be expressed as a linear combination of them.

If the spectrum is continuous then the eigenfunctions are orthogonal and normalizable in a "Dirac delta sense."
We will call them Dirac delta normalizable functions. These functions do not belong to $L^2 (R)$ strictly but are useful.

E.g. Find the eigen-values and eigenfunctions of the momentum operator.

Solution: Let $f_p (x)$ be the solutions.

$\Rightarrow \quad -i\hbar \frac{df_p (x)}{dx} = p f_p (x)$

$\Rightarrow \quad -i\hbar \int df_p = p \int dx$

$\Rightarrow \quad -i\hbar \ln \left[ \frac{f_p (x)}{f_p (x_0)} \right] = p(x-x_0)$

where $x_0 = \text{constant}$

$\Rightarrow \quad f_p (x) = A e^{\frac{i}px}, \text{ where } A = \text{constant}$.

Note $\int |f_p (x)|^2 dx = 1A^2 \int_{-\infty}^{\infty} \frac{e^{-\frac{1}{\hbar} x}}{\sqrt{2\pi \hbar}} dx = 1A^2 \int_{-\infty}^{\infty} e^{-\frac{2\pi}{\hbar}|p-p'|} dy = 2\pi \hbar 1A^2 \delta(p-p')$

Choose $A = (2\pi \hbar)^{-\frac{1}{2}} = \hbar^{-\frac{1}{2}}$

$\Rightarrow \quad f_p (x) = \frac{e^{\frac{i}px}}{\sqrt{2\pi \hbar}}$ and $\langle f_{p'} | f_p \rangle = \delta(p-p')$

since $\int_{-\infty}^{\infty} f_{p'}^*(x) f_p (x) dx = \delta(p-p')$. 
Thus \( \{ f_p(x), p \in \mathbb{R} \} \) form an orthonormal set in the Dirac delta sense. Any function \( \psi(x) \) may be expanded as

\[
\psi(x) = \int_{-\infty}^{\infty} c(p) f_p(x) \, dp = \int_{-\infty}^{\infty} \frac{c(p)}{\sqrt{2\pi \hbar}} e^{-i px} \, dp
\]

\( c(p) \) can now be found as follows,

\[
\int_{-\infty}^{\infty} \frac{e^{-i px}}{\sqrt{2\pi \hbar}} \psi(x) \, dx = \langle f_p | \psi \rangle
\]

\[
= \int_{-\infty}^{\infty} dp \, c(p) \int_{-\infty}^{\infty} \frac{e^{-i px} \, dx}{\sqrt{2\pi \hbar}} = \int_{-\infty}^{\infty} \frac{c(p) \delta(p-p')}{\sqrt{2\pi \hbar}} \, dp
\]

\[
= c(p')
\]

\[
\Rightarrow c(p) = \langle f_p | \psi \rangle = \int_{-\infty}^{\infty} \frac{e^{-i px}}{\sqrt{2\pi \hbar}} \psi(x) \, dx
\]

\[
= \int_{-\infty}^{\infty} f_p^*(x) \psi(x) \, dx
\]

E.g., Find the eigenvalues and eigenfunctions of the position operator:

\[
\text{Solution: Let } g_y(x) \text{ be the eigenfunction with eigenvalue } y:
\]

\[
\Rightarrow x g_y(x) = y g_y(x)
\]
This is true only when \( g_y(x) = \delta(x-y) \).

Now \( \int_{-\infty}^{\infty} \hat{g}_y(x) g_y(x) \, dx = A^2 \int_{-\infty}^{\infty} \delta(x-y) \delta(x-y) \, dx = A^2 \delta(y-y') \).

Choose \( A = 1 \) \( \Rightarrow g_y(x) = \delta(x-y) \).

The set \( \{g_y(x), y \in \mathbb{R}\} \) forms a Dirac delta orthonormal set.

We can expand \( \Psi(x) = \int_{-\infty}^{\infty} c(y) \delta(x-y) \, dy \).

\( \Rightarrow \int_{-\infty}^{\infty} \delta(y'-x) \Psi(x) \, dx = \int_{-\infty}^{\infty} c(y) \, dy \int_{-\infty}^{\infty} \delta(x-y') \delta(x-y) \, dx = \int_{-\infty}^{\infty} c(y) \delta(y-y') \, dy = c(y') \).

\( \Rightarrow c(y) = \left( \frac{g_y}{\Psi} \right)^* \Psi(x) = \Psi(y) \).

\( \Rightarrow \Psi(x) = \int_{-\infty}^{\infty} \Psi(y) \delta(x-y) \, dy \).

**Question:** Solve the TDSE for a potential \( V(x) \) which gives only a discrete energy spectrum \( \{E_n, n \in \mathbb{N}\} \). The initial wavefunction is \( \Psi(x,0) = \Psi_0(x) \).

**Answer:** Let the solution be \( \Psi(x,t) \). TDSE gives then \( \frac{i}{\hbar} \partial \Psi(x,t) = \hat{H} \Psi(x,t) \).
Try a solution \( \psi_t(x,t) = \psi(x) \phi(t) \)

TDSE now gives for \( \psi_t \)

\[
\dot{\psi}(x) \phi(t) = \hat{H} \psi(x) \phi(t)
\]

Note \( \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \)

\( \Rightarrow \dot{\psi}(x) \phi(t) = \phi(t) \hat{H} \psi(x) \)

\( \Rightarrow \frac{\dot{\psi}(x)}{\phi(t)} = \frac{\hat{H} \psi(x)}{\phi(t)} = \psi(x) \)

This will hold true \( \forall x, t \) iff

\[
\dot{\phi}(t) = E = \text{constant}
\]

\[
\phi(t) = Ae^{-\frac{2\pi i E t}{\hbar}}, \ A = \text{constant}
\]

Also \( \hat{H} \psi(x) = E \psi(x) \)

This equation is called the time independent Schrödinger equation \( \hat{H} (TISE) \).

It is given that \( E \) takes discrete values \( E_n \). The corresponding eigenvalues \( \hat{\psi} \) eigenvectors are \( \psi_n(x) \)

\( \Rightarrow \hat{H} \psi_n(x) = E_n \psi_n(x) \) are the solutions.
\( E_n \) are the eigen energies.

\[
\Psi_n(x, t) = c_n \psi_n(x) e^{-\frac{i E_n t}{\hbar}}, \quad c_n = \text{constant.}
\]

Hence the general solution will be

\[
\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-\frac{i E_n t}{\hbar}}
\]

Note \( \hat{H} \) is Hermitian \( \iff \psi_n \in \mathbb{R} \) and

\[
\int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) \, dx = \langle \psi_m | \psi_n \rangle = \delta_{m,n}.
\]

We have not determined \( c_n \) yet. Here we use the initial condition that \( \Psi(x, 0) \) is known. It is \( \psi_0(x) \).

\[
\Psi(x, 0) = \sum_n c_n \psi_n(x)
\]

\[
c_n = \int_{-\infty}^{\infty} \psi_n^*(x) \psi_0(x) \, dx
\]

\[
\Psi(x, t) = \sum_n \psi_n(x) e^{-\frac{i E_n t}{\hbar}} \int_{-\infty}^{\infty} \psi_n(y) \psi_0(y) \, dy
\]

\[
= \left[ \sum_n \int_{-\infty}^{\infty} \psi_n(y) \psi_n^*(x) e^{-\frac{i E_n t}{\hbar}} \right] \psi_0(y)
\]

\[
= \hat{U}(x, t; y, 0) \psi_0(y)
\]

where \( \hat{U} \) is called the propagator of the TISE.