# Probability Theory

[DISCRETE CASE]

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

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

$$\therefore \quad N \equiv \sum_{i \in I} N_i$$

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

$$P(V_i) \equiv N_i / N$$

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

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

The average value of $V$ denoted by $\langle V \rangle$ is also known as its expectation value. It is defined as

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

The variance ($\sigma^2$) of $V$ is defined by

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

$$\therefore \sigma^2 = \langle V^2 + \langle V \rangle^2 - 2V\langle V \rangle \rangle \qquad \boxed{3\text{-}2}$$

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

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

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

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

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

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

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

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

$$\sigma \equiv \sqrt{\langle (V - \langle V \rangle)^2 \rangle} \equiv \sqrt{\sigma^2}$$

Note also that $\sigma^2 \geq 0$

$$\Rightarrow \langle v^2 \rangle \geq \langle v \rangle^2$$

[CONTINUUM CASE]

If $v$ is a continuous variable and measurement of $v$ can give any real value, i.e. $v \in R$, then the probability $P(v_0)$ of finding any fixed and <u>exact</u> value $v_0$

$$P(v_0) = 0 \quad , \forall v_0 \in R.$$

However if we define $P(v_0)$ as the probability of finding a value of $v$ between $v_0$ and $v_0 + dv$ then

$$P(v_0) = \rho(v_0)\, dv \quad , \quad v_0 \in R$$

where $\rho(v)$ is called the probability density of $v$. Note that

$$\int_{v \in R} \rho(v)\, dv = 1$$

$\Rightarrow$ $\rho(v)$ has dimensions of $1/v$.

Probability of $v$ being in an interval $[v_1, v_2]$, $v_2 > v_1$ is

$$P(v \in [v_1, v_2]) = \int_{v_1}^{v_2} \rho(v)\, dv$$

Also $$\langle f(v) \rangle = \int_{v \in R} f(v)\rho(v)\, dv$$

$$\sigma^2 \equiv \int_{v \in R} (v - \langle v \rangle)^2 \rho(v)\, dv$$

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

$$= \int_v v^2 \rho(v)\, dv - \left[ \int_v v\rho(v)\, dv \right]^2$$

$$\sigma = \sqrt{\sigma^2}$$

Most probable value happens when $\rho(v)$ is maximum

$$\Rightarrow \left. \frac{d\rho(v)}{dv} \right|_{v=v_m} = 0 \quad \text{and}$$

$$\left. \frac{d^2\rho}{\partial v^2} \right|_{v=v_m} < 0$$

# 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 ~~the~~ QM of only one particle.

| CM | QM |
|---|---|
| I] The state of a particle at time $t$ is defined by its position $x(t)$ and momentum $p(t) \equiv m\frac{dx(t)}{dt} \equiv m\dot{x}(t)$ i.e. as a point in phase space $(x(t), p(t))$ | I] The state of a particle is defined by a wavefunction $\Psi(x,t)$ in Hilbert space ($\mathcal{HS}$). $\mathcal{HS}$ is the space of all square-integrable functions. $f(x) \ni \int_{-\infty}^{\infty} \lvert f(x)\rvert^2 dx \in R$. |
| II] Every dynamical variable $\omega$ is a function of $x$ and $p$, i.e. $\omega = \omega(x,p)$. e.g. kinetic energy $T = \frac{m}{2}v^2 = \frac{p^2}{2m}$, potential energy $V = V(x)$. | II] The independent variables $x$ and $p$ of CM are represented by operators $\hat{X}$ and $\hat{P}$. They have forms $\hat{X} \equiv x$ and $\hat{P} \equiv -i\hbar\frac{d}{dx}$. The operators $\hat{\Omega}(\hat{X}, \hat{P})$ corresponding to classical |

dependent variables $\omega(x,p)$ are Hermitian operators. $\hat{X}$ and $\hat{P}$ are also Hermitian.

e.g. since $T = \dfrac{p^2}{2m}$



$$\hat{T} \equiv \left(-i\hbar \frac{d}{dx}\right)^2 = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

III] 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.

III] Let the state of the particle be given by $\Psi(x,t)$. Let $\hat{\Omega}_D$ 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 $\hat{\Omega}_D \phi_n(x) = \omega_n \phi_n(x)$

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

$$P(\omega_n) \propto |c_n(t)|^2$$

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 $\hat{\Omega}_c$ with a continuous eigen-spectrum $\beta$ we get

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

$$\hat{\Omega}_C\,\phi_\beta(x) = \beta\,\phi_\beta(x)$$

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

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

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

As a result of the measurement of $\hat{\Omega}_D$ the state of the system will change to $\phi_n(x)$ from $\Psi(x)$.
For measurement of $\hat{\Omega}_c$ it will change to $\phi_\beta(x)$ from $\Psi(x)$.
This is called the "Measurement" or "Collapse" Postulate of QM.

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

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

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hat{H}\,\Psi(x,t)$$

$$\dot{x} = \frac{\partial H_c(x,p)}{\partial p} \text{ and}$$

$$\dot{p} = -\frac{\partial H_c(x,p)}{\partial x}$$

$$H_c = T + V = \frac{p^2}{2m} + V(x)$$

$$\dot{x} = \frac{\partial H}{\partial p} = p/m$$

is just the velocity

$$\dot{p} \equiv \frac{dp}{dt} = ma = -\frac{\partial V(x)}{\partial x}$$

$$\Rightarrow ma = -\frac{dV(x)}{dx} = F$$

is Newton's second law.

where $\hat{H} = \hat{H}(\hat{x}, \hat{P}) = H_c(x \to \hat{x}, p \to \hat{P})$

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



$$H_c = \frac{p^2}{2m} + V(x) \text{ then}$$

$$\hat{H} = \frac{\hat{P}^2}{2m} + \hat{V}(\hat{X})$$

$$= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x).$$

TDSE $\equiv$ time dependent Schrödinger equation.

$h \equiv$ Planck's constant

$\hbar \equiv h/(2\pi)$

$h = 6.63 \times 10^{-34}$ Joule second

$= 6.63 \times 10^{-34}\ kg.\frac{m^2}{s}$

$[h] \equiv [M^1 L^2 T^{-2}]$

The inner product of two functions $f(x)$ and $g(x)$ is defined as

$$\langle f | g \rangle = \int_a^b f^*(x)\, g(x)\, dx$$ over the interval $[a, b]$.

Note $[\langle f | g \rangle]^* = \langle g | f \rangle$.

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

$$\langle f | \hat{\varphi} f \rangle = \langle \hat{\varphi} f | f \rangle \;, \quad \forall\, |f\rangle$$

i.e. $$\int_a^b f^*(x)\, \hat{\varphi}\, f(x)\, dx = \int_a^b [\hat{\varphi} f(x)]^* f(x)\, dx$$

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 $\hat{\varphi}$ with eigenvalue $q$.

$$\Rightarrow \quad \hat{\varphi} f_q(x) = q\, f_q(x)$$

$$\hat{\varphi} \text{ is Hermitian} \Rightarrow q^* = q \Rightarrow q \in R.$$

Eigenvalues of a Hermitian operator are therefore always real.

Two functions are said to be orthogonal if their inner product~~s~~ ~~are~~ is zero.

f and g are orthogonal $\Leftrightarrow$

$$\langle f|g\rangle = \langle g|f\rangle = 0.$$

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

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

$\hat{Q}$ is Hermitian $\Rightarrow \langle f|\hat{Q} g\rangle = \langle \hat{Q} f|g\rangle$

$$\Rightarrow q'\langle f|g\rangle = q^{*}\langle f|g\rangle$$

$$q', q \in R \Rightarrow q^{*} = q$$

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

The eigenfunctions of an observable (Hermitian) operator are complete. I.e. any function in HS 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 HS strictly but are useful.

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

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

3-11

$$\therefore \quad -i\hbar \frac{d}{dx} f_p(x) = p\, f_p(x)$$

$$\Rightarrow \quad -i\hbar \int \frac{df_p}{f_p} = p \int dx$$

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

where $x_0$ = constant

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

Note $\int_{-\infty}^{\infty} |f_p(x)|^2 dx = |A|^2 [\infty] = \infty$

$$\int_{-\infty}^{\infty} f_{p'}^*(x) f_p(x)\, dx = |A|^2 \int_{-\infty}^{\infty} e^{\frac{i(p-p')x}{\hbar}} dx$$

$$= |A|^2 \hbar \int_{-\infty}^{\infty} e^{iy(p-p')} dy = 2\pi\hbar\, |A|^2\, \delta(p-p')$$

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

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

since $\int_{-\infty}^{\infty} f_{p'}(x) f_p(x)\, dx = \delta(p-p')$.

Thus $\{f_p(x), p \in R\}$ form an orthonormal set in the Dirac delta sense. Any function $\Psi(x)$ may be expanded as

$$\Psi(x) = \int_{-\infty}^{\infty} c(p) f_p(x)\, dp = \int_{-\infty}^{\infty} \frac{c(p)}{\sqrt{2\pi\hbar}} e^{ipx} dp$$

$c(p)$ can now be found as follows.

$$\int_{-\infty}^{\infty} \frac{e^{-ip'x}}{\sqrt{2\pi\hbar}} \Psi(x)\, dx = \langle f_{p'} | \Psi \rangle$$

$$= \int_{-\infty}^{\infty} \frac{dp\, c(p)}{(2\pi\hbar)} \int_{-\infty}^{\infty} e^{i(p-p')x} dx = \int_{-\infty}^{\infty} c(p)\, \delta(p-p')\, dp$$

$$= c(p')$$

$$\Rightarrow c(p) = \langle f_p | \Psi \rangle = \int_{-\infty}^{\infty} \frac{e^{-ipx}}{\sqrt{2\pi\hbar}} \Psi(x)\, dx$$

$$= \int_{-\infty}^{\infty} f_p^*(x) \Psi(x)\, dx.$$

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

Solution: $\longrightarrow$ Let $g_y(x)$ be the eigenfunction with eigenvalue $y$.

$$\Rightarrow x\, g_y(x) = y\, g_y(x)$$

This is true only when $g_y(x) = \delta(x-y)\,A$

Now $\int_{-\infty}^{\infty} g_{y'}^*(x)\, g_y(x)\, dx = |A|^2 \int_{-\infty}^{\infty} \delta(x-y')\delta(x-y)\, dx$

$= |A|^2\, \delta(y-y')$

3-13

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

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

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

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

$$= \int_{-\infty}^{\infty} c(y)\, \delta(y-y')\, dy = c(y')$$

$$\Rightarrow c(y) = \langle g_y | \Psi \rangle = \Psi(y)$$

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

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

Answer :→ Let the solution be $\Psi(x,t)$. TDSE gives then

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hat{H}\Psi(x,t).$$

Try a solution $\Psi_t(x,t) = \Psi(x)\varphi(t)$

TDSE now gives for $\Psi_t$

$$i\hbar \Psi(x)\dot{\varphi}(t) = \hat{H}\Psi(x)\varphi(t)$$

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

$$\Rightarrow \; i\hbar \Psi(x)\dot{\varphi}(t) = \varphi(t)\hat{H}\Psi(x)$$

$$\Rightarrow \; i\hbar \frac{\dot{\varphi}(t)}{\varphi(t)} = \frac{\hat{H}\Psi(x)}{\Psi(x)}$$

This will hold true $\forall x, t$ iff

$$i\hbar \frac{\dot{\varphi}(t)}{\dot{\varphi}(t)} = E = \text{constant}$$

$$\Rightarrow \; \varphi(t) = A e^{\frac{-iEt}{\hbar}} \text{, } A = \text{constant}$$

Also $\hat{H}\Psi(x) = E\Psi(x)$

This equation is called the time independent Schrödinger equation ~~ID~~ (TISE).
It is given that $E$ takes ~~disc~~ discrete values $E_n$. The corresponding ~~eigenvalues~~ ~~(EV)~~ eigenvectors are $\Psi_n(x)$

$$\Rightarrow \; \hat{H}\Psi_n(x) = E_n\Psi_n(x) \text{ are the solutions.}$$

$E_n$ are the eigen energies.

$$\therefore \quad \Psi_{t,n}(x,t) = c_n \Psi_n(x) e^{\frac{-iE_n t}{\hbar}}, \quad c_n = \text{constant}.$$

Hence the general solution will be

$$\Psi(x,t) = \sum_n c_n \Psi_n(x) e^{\frac{-iE_n t}{\hbar}}$$

Note $\hat{H}$ is Hermition $\Rightarrow E_n \in R$ 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 $\Psi_i(x)$.

$$\therefore \quad \Psi_i(x) = \sum_n c_n \Psi_n(x)$$

$$\Rightarrow \quad c_n = \int_{-\infty}^{\infty} \Psi_n^*(x) \Psi_i(x) dx$$

$$\Rightarrow \quad \Psi(x,t) = \sum_n \Psi_n(x) e^{\frac{-iE_n t}{\hbar}} \int_{-\infty}^{\infty} \Psi_n^*(y) \Psi_i(y) dy$$

$$= \left[ \sum_n \int_{-\infty}^{\infty} dy \, \Psi_n^*(y) \Psi_n(x) e^{\frac{-iE_n t}{\hbar}} \right] \Psi_i(y)$$

$$= \hat{U}(x,t;y,0) \Psi_i(y)$$

where $\hat{U}$ is called the propogator of the TDSE.