

Lecture-XXIII

Quantum Mechanics-Schrodinger Equation

How to study QM?

Classically the state of a particle is defined by (x,p) and the dynamics is given by Hamilton's equations

$$\text{Hamiltonian: } H = \frac{p^2}{2m} + V(x) = K + V$$
$$\dot{x} = \frac{\partial H}{\partial p_i}, \quad \dot{p} = -\frac{\partial H}{\partial x_i}$$

What is a quantum mechanical state?

Coordinate and momentum is not complete in QM, needs a probabilistic predictions.

The **wave function** associated with the particle can represent its state and the dynamics would be given by **Schrodinger equation**.

However, wave function is a complex quantity!

Need to calculate the probability and the expectation values.

The Schrodinger equation:

Given the initial state $\psi(x,0)$, the Schrodinger equation determines the states $\psi(x,t)$ for all future time

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi = H \Psi$$

where H is the Hamiltonian of the system.

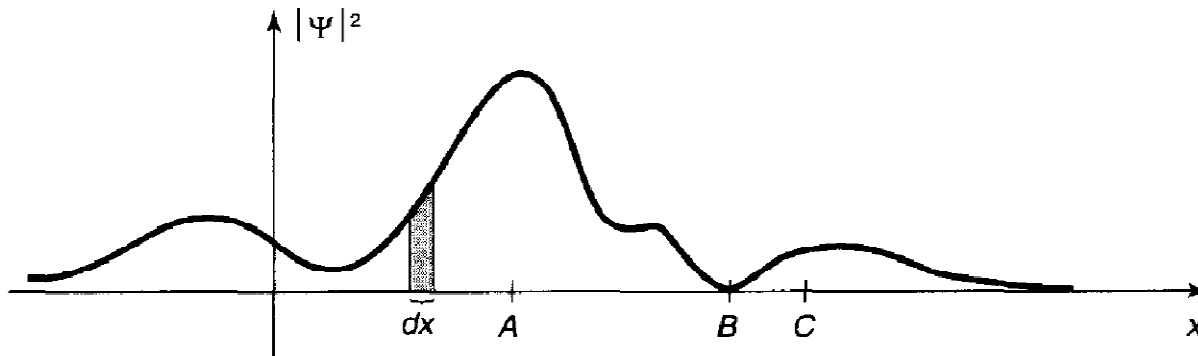
	Classical	Quantum
Hamiltonian	$H = \frac{p^2}{2m} + V(x)$	$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$

But what exactly is this "wave function", and what does it mean? After all, a particle, by its nature, is localized at a point, whereas the wave function is spread out in space (it's a function of x , for any given time t). How can such an object be said to describe the state of a particle?

Born's statistical interpretation of $\Psi(x, t)$:

$|\Psi(x, t)|^2 dx$ gives the probability of finding the particle between x and $x+dx$, at time t or, more precisely,

$$|\Psi(x, t)|^2 dx = \left\{ \begin{array}{l} \text{probability of finding the particle} \\ \text{between } x \text{ and } (x + dx), \text{ at time } t. \end{array} \right\}$$



A typical wave function. The particle would be relatively likely to be found near A, and unlikely to be found near B. The shaded area represents the probability of finding the particle in the range dx .

The probability $P(x, t)$ of finding the particle in the region lying between x and $x+dx$ at the time t , is given by the squared amplitude $P(x, t) dx = |\Psi(x, t)|^2 dx$

Probability: A few definitions

Because of the statistical interpretation, probability plays a central role in quantum mechanics. The probability that x lies between a and b (a finite interval) is given by the integral of $\rho(x)$, the probability density function:

$$P_{ab} = \int_a^b \rho(x) dx,$$

The sum of all the probabilities is 1: $\int_{-\infty}^{+\infty} \rho(x) dx = 1,$

The average value of x : $\langle x \rangle = \int_{-\infty}^{+\infty} x \rho(x) dx,$

The average of a function of x : $\langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x) \rho(x) dx,$

Standard deviation: $\sigma^2 \equiv \langle (\Delta x)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2. \quad \Delta x = x - \langle x \rangle$

Some handy Integrals

$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a} \right)^{1/2}$$

$$\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4a} \left(\frac{\pi}{a} \right)^{1/2}$$

$$\int_0^{\infty} x^4 e^{-ax^2} dx = \frac{3}{8a^2} \left(\frac{\pi}{a} \right)^{1/2}$$

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a} \right)^{1/2}$$

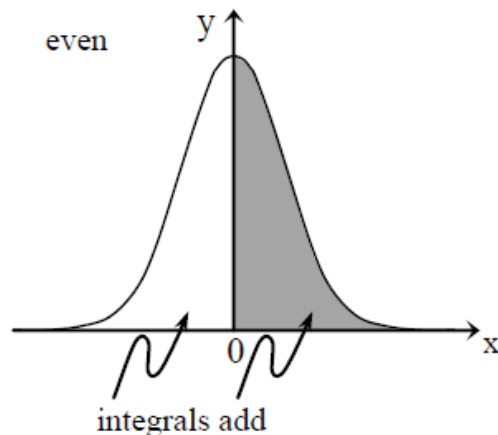
$$\int_0^{\infty} x e^{-ax^2} dx = \frac{1}{2a}$$

$$\int_0^{\infty} x^3 e^{-ax^2} dx = \frac{1}{2a^2}$$

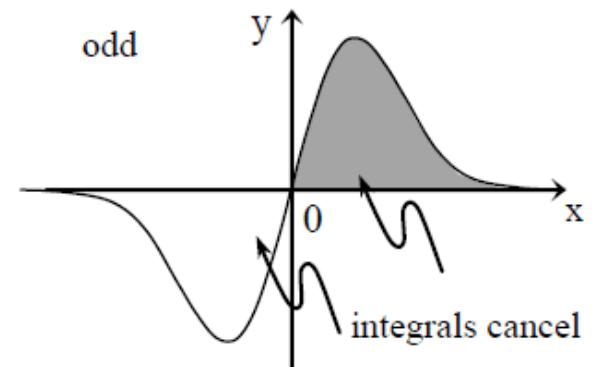
$$\int_0^{\infty} x^5 e^{-ax^2} dx = \frac{1}{a^3}$$

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2} \left(\frac{1}{a^{n+1}} \right)$$

Laplace in 1778 proved that $\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$



$$\int_{-\infty}^{+\infty} x^{2n} e^{-ax^2} dx = 2 \int_0^{\infty} x^{2n} e^{-ax^2} dx$$



$$\int_{-\infty}^{+\infty} x^{2n+1} e^{-ax^2} dx = 0$$

Gaussian distribution

Consider the Gaussian distribution $\rho(x) = Ae^{-\lambda(x-a)^2}$, where A , a , and λ are constants. (a) Determine A , (b) Find $\langle x \rangle$, $\langle x^2 \rangle$, and σ , (c) Sketch the graph of $\rho(x)$.

(a) $1 = \int_{-\infty}^{\infty} Ae^{-\lambda(x-a)^2} dx$. Let $u \equiv x - a$, $du = dx$, $u : -\infty \rightarrow \infty$.

$$1 = A \int_{-\infty}^{\infty} e^{-\lambda u^2} du = A \sqrt{\frac{\pi}{\lambda}} \Rightarrow \boxed{A = \sqrt{\frac{\lambda}{\pi}}}$$

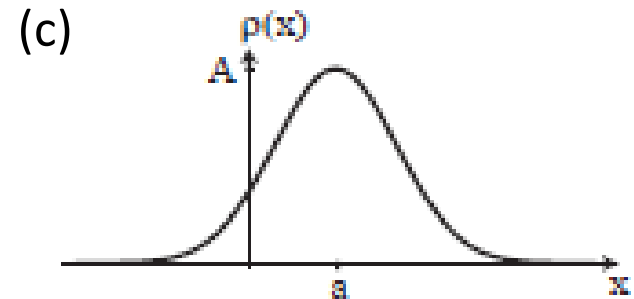
(b)

$$\begin{aligned} \langle x \rangle &= A \int_{-\infty}^{\infty} x e^{-\lambda(x-a)^2} dx = A \int_{-\infty}^{\infty} (u + a) e^{-\lambda u^2} du \\ &= A \left[\int_{-\infty}^{\infty} u e^{-\lambda u^2} du + a \int_{-\infty}^{\infty} e^{-\lambda u^2} du \right] = A \left(0 + a \sqrt{\frac{\pi}{\lambda}} \right) = \boxed{a}. \end{aligned}$$

$$\begin{aligned} \langle x^2 \rangle &= A \int_{-\infty}^{\infty} x^2 e^{-\lambda(x-a)^2} dx \\ &= A \left\{ \int_{-\infty}^{\infty} u^2 e^{-\lambda u^2} du + 2a \int_{-\infty}^{\infty} u e^{-\lambda u^2} du + a^2 \int_{-\infty}^{\infty} e^{-\lambda u^2} du \right\} \\ &= A \left[\frac{1}{2\lambda} \sqrt{\frac{\pi}{\lambda}} + 0 + a^2 \sqrt{\frac{\pi}{\lambda}} \right] = \boxed{a^2 + \frac{1}{2\lambda}}. \end{aligned}$$

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = a^2 + \frac{1}{2\lambda} - a^2 = \frac{1}{2\lambda};$$

$$\boxed{\sigma = \frac{1}{\sqrt{2\lambda}}}.$$



Normalization of $\psi(x,t)$:

$|\Psi(x, t)|^2$: is the probability density for finding the particle at point x , at time t .

Because the particle must be found somewhere between $x=-\infty$ and $x=+\infty$ the wave function must obey the normalization condition

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1.$$

Without this, the statistical interpretation would be meaningless. Thus, there is a multiplication factor. However, the wave function is a solution of the Schrodinger eq:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi.$$

Therefore, one can't impose an arbitrary condition on ψ without checking that the two are consistent.

Interestingly, if $\psi(x, t)$ is a solution, $A\psi(x, t)$ is also a solution where A is any (complex) constant.

Therefore, one must pick a undetermined multiplicative factor in such a way that the Schrodinger Equation is satisfied. This process is called **normalizing** the wave function.

For some solutions to the Schrodinger equation, the integral is infinite; in that case no multiplicative factor is going to make it 1. The same goes for the trivial solution $\psi = 0$. Such non-normalizable solutions cannot represent particles, and must be rejected.

Physically realizable states correspond to the "square-integrable" solutions to Schrodinger's equation.

What all you need is that
$$\int_{-\infty}^{\infty} dx |\psi(x, 0)|^2 < \infty$$

that is, the initial state wave functions must be square integrable.

Since we may need to deal with integrals of the type

$$\int_{-\infty}^{\infty} dx \psi^*(x, t) x^n \psi(x, t)$$

you will require that the wave functions $\psi(x, 0)$ go to zero rapidly as $x \rightarrow \pm\infty$ often faster than any power of x .

We shall also require that the wave functions $\psi(x, t)$ be continuous in x .

The Importance of Phases

The emphasis on $|\psi(x, t)|^2$ as the physically relevant quantity might lead to the impression that the *phase* of the wave function is of no importance. If we write $\psi = Re^{i\theta}$, then indeed $|\psi|^2 = R^2$ independent of θ . However, the linearity of the equation allows us to add solutions, as in our discussion of the electron interference pattern with two slits. We see that

$$|R_1 e^{i\theta_1} + R_2 e^{i\theta_2}|^2 = R_1^2 + R_2^2 + 2R_1 R_2 \cos(\theta_1 - \theta_2)$$

depends on the relative phase. An overall phase in the total wave function can be ignored, or chosen arbitrarily for convenience.

Example 1: A particle is represented by the wave function $\psi = Ae^{i\omega t}e^{-x^2/2a^2}$ where A , ω and a are real constants. The constant A is to be determined.

$$1 = \int_{-\infty}^{\infty} \psi^* \psi dx = A^2 \int_{-\infty}^{\infty} e^{-i\omega t} e^{i\omega t} e^{-x^2/a^2} dx$$

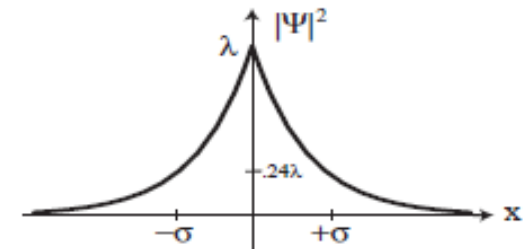
$$= A^2 a \int_{-\infty}^{\infty} e^{-\eta^2} d\eta = A^2 a \sqrt{\pi}$$

The normalized wave-function is therefore : $\psi = \frac{1}{a^{1/2}\pi^{1/4}} e^{i\omega t} e^{-x^2/2a^2}$

Example 2: Consider the wave function $\Psi(x, t) = Ae^{-\lambda|x|}e^{-i\omega t}$, where A , λ , and ω are Positive real constants. Normalize ψ . Sketch the graph of $|\psi|^2$ as a function of x .

$$1 = \int |\Psi|^2 dx = 2|A|^2 \int_0^{\infty} e^{-2\lambda x} dx = 2|A|^2 \left(\frac{e^{-2\lambda x}}{-2\lambda} \right) \Big|_0^{\infty} = \frac{|A|^2}{\lambda}; \quad \boxed{A = \sqrt{\lambda}}$$

$$|\Psi(\pm\sigma)|^2 = |A|^2 e^{-2\lambda\sigma} = \lambda e^{-2\lambda\sigma}$$



Example 3: Normalize the wave function $\psi = Ae^{i(\omega t - kx)}$, where A , k and ω are real positive constants.

$$1 = \int_{-\infty}^{+\infty} \psi \psi^* dx = |A|^2 \int_{-\infty}^{+\infty} dx \rightarrow \infty \quad 1 = \int_{-L}^{+L} \psi \psi^* dx = |A|^2 \int_{-L}^{+L} dx = |A|^2 2L$$

!?

Does ψ remain normalized forever?

Suppose we have normalized the wave function at time $t = 0$. How do we know that it will *stay* normalized, as time goes on and $\Psi(x, t)$ evolves?

$$\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} |\Psi(x, t)|^2 dx. \quad \text{[Note that the integral is a function only of } t, \text{ but the integrand is a function of } x \text{ as well as } t.\text{]}$$

By the product rule, $\frac{\partial}{\partial t} |\Psi|^2 = \frac{\partial}{\partial t} (\Psi^* \Psi) = \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi$

The Schrodinger equation and its complex conjugate are

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi, \quad \text{and} \quad \frac{\partial \Psi^*}{\partial t} = -\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^*$$

So, $\frac{\partial}{\partial t} |\Psi|^2 = \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) = \frac{\partial}{\partial x} \left[\frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \right]$

Then, $\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \Big|_{-\infty}^{+\infty} = 0$

$$J(x, t) \equiv \frac{i\hbar}{2m} \left(\Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right)$$

Is the probability current.

Since $\Psi(x, t)$ must go to zero as x goes to $(\pm)$ infinity--otherwise the wave function would not be normalizable. Thus, if the wave function is normalized at $t = 0$, it stays normalized for all future time.

The Schrodinger equation has the property that it automatically preserves the normalization of the wave function--without this crucial feature the Schrodinger equation would be incompatible with the statistical interpretation.

Probability current

If $P_{ab}(t)$ be the probability of finding the particle in the range $(a < x < b)$, at time t , then

$$\frac{dP_{ab}}{dt} = J(a, t) - J(b, t) \quad \text{where} \quad J(x, t) \equiv \frac{i\hbar}{2m} \left(\Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right).$$

$$P_{ab}(t) = \int_a^b |\Psi(x, t)|^2 dx, \quad \text{so } \frac{dP_{ab}}{dt} = \int_a^b \frac{\partial}{\partial t} |\Psi|^2 dx.$$

$$\frac{\partial}{\partial t} |\Psi|^2 = \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) = \frac{\partial}{\partial x} \left[\frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \right]$$

$$\therefore \frac{dP_{ab}}{dt} = - \int_a^b \frac{\partial}{\partial x} J(x, t) dx = - [J(x, t)]|_a^b = J(a, t) - J(b, t).$$

Probability is dimensionless, so J has the dimensions 1/time, and units second⁻¹

Example 1: Take $\Psi(x, t) = f(x)e^{-iat}$, where $f(x)$ is a real function.

$$\text{So } \Psi \frac{\partial \Psi^*}{\partial x} = f e^{-iat} \frac{df}{dx} e^{iat} = f \frac{df}{dx}, \quad \text{and} \quad \Psi^* \frac{\partial \Psi}{\partial x} = f \frac{df}{dx}$$

$$J(x, t) \equiv \frac{i\hbar}{2m} \left(\Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right) = 0.$$

$$\frac{dP_{ab}}{dt} = J(a, t) - J(b, t) = 0. \quad \text{for any } a \text{ and } b.$$

Example 2: Take $\psi = Ae^{i(\omega t - kx)}$, where A , k and ω are real positive constants.

$$\psi = Ae^{i(\omega t - kx)}, \text{ then } \psi^* = Ae^{-i(\omega t - kx)}$$

$$\text{So, } \psi \frac{\partial \psi^*}{\partial x} = Ae^{i(\omega t - kx)} (ik) Ae^{-i(\omega t - kx)} = ikA^2, \quad \text{and} \quad \psi^* \frac{\partial \psi}{\partial x} = Ae^{-i(\omega t - kx)} (-ik) Ae^{i(\omega t - kx)} = -ikA^2$$

$$\text{Therefore, } J(x, t) = \frac{i\hbar}{2m} (2ikA^2) = -\frac{\hbar k}{m} A^2$$

$$\frac{dP_{ab}}{dt} = J(a, t) - J(b, t) = 0. \quad \text{for any } a \text{ and } b.$$

Thus, once it is normalized, it will remain normalized.