

Wavefunction

Having seen various aspects of objects in microscopic world, one must be convinced that the physical description of those look very different from the objects that we deal with in day-to-day (macroscopic) world. For instance, objects in microscopic world (like atoms, electrons etc) display some features of a wave too. Moreover, measurement of position and momentum has severe restrictions on their accuracy. In contrast, a measurement of position and momenta of objects we see in macroscopic world face no such restrictions. These restrictions are statistical in nature, as explained at the end of the previous section. This requires us to seek a description of objects in microscopic world that is inherently statistical or probabilistic. We will introduce this description after explaining the important aspects of measurement of physical quantities.

Description of the state of a microscopic object like an electron or an atom is completely counter intuitive. We will learn how this is by looking at how the position of, say, an electron is measured. To highlight the counter intuitive description of this measurement, it is better to see it in contrast with the measurement of position of a macroscopic object.

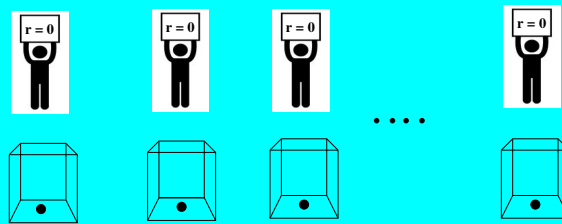


Fig 1: Measuring positions of tennis balls

Let us consider a large number N of identical tennis balls that weigh approximately 60 gms all placed at the same position, say $\mathbf{r} = 0$, with no momentum inside identical cubical containers as shown in fig(1). If we ask N observers to come and record the positions of these balls at a given instant of time t they would all record the position as $\mathbf{r} = 0$, if the tennis balls or the containers are not experiencing any force. This is just what we expect from our day-to-day experience with such objects of a few grams of mass. If the tennis balls were provided with the same initial momentum \mathbf{p} , the N observers would record the positions of the tennis balls at time t to be some \mathbf{r}' , same for all the balls.

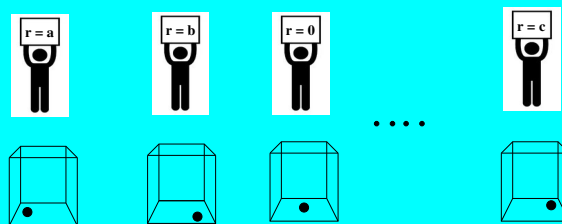


Fig 2: Measuring positions of electrons

Let us now repeat the same with electrons as shown in fig(2). If we place electrons at the same position with same momentum ¹inside the containers and repeat the measurement process

described above, we would see that all the N observers do not record the same positions for the electrons in their respective containers. While a certain set of observers record one range of values of position another bunch of observers record a different range of values and so on are the result of the measurement. Using this data one can actually find what is the probability for finding the particle in a certain position interval. This randomness is an inherent aspect of measurement on microscopic objects. This aspect holds true not just for measurement of position but, in general, for every physical quantity that can be measured. However, if the particle is in certain “special” states called *eigenstates* all the observers will read the same value for some physical quantities being measured.

Due to the inherent randomness in the outcome of a measurement, the state of physical systems like electrons and atoms are specified by a function of position and time $\psi(\mathbf{r}, t)$ called *wavefunction*.

In what follows, we will assume that the particle to be one that moves only on a line, ie., in one dimension. We will choose this line to be X-axis. Thus the state of this particle will be provided by a wavefunction that depends only on X-coordinate : $\psi(x, t)$. Wavefunction is a complex function and thus has a real part and an imaginary part both being independent functions of position and time :

$$\psi(x, t) = \psi_1(x, t) + i\psi_2(x, t) \quad \text{where } i = \sqrt{-1}$$

Wavefunction has a physical meaning : square of its modulus, $|\psi(x, t)|^2 = \psi^*(x, t)\psi(x, t)$, is the probability density (meaning, probability per unit length) for finding the particle. Therefore the probability for finding the particle in the interval $(x, x + dx)$ is

$$dx |\psi(x, t)|^2$$

The probability to find the particle between points $x = x_1$ and $x = x_2$ is

$$\int_{x_1}^{x_2} dx |\psi(x, t)|^2 \tag{1}$$

Since the particle has to exist on the X-axis, the probability to find the particle on the entire X-axis ($-\infty \leq x \leq \infty$) must be ONE.

$$\int_{-\infty}^{\infty} dx |\psi(x, t)|^2 = 1 \tag{2}$$

The condition in eqn(2) is the *normalization condition* for the wavefunction.

Example 1:

The wavefunction of a particle is given by

$$\psi(x, t) = \begin{cases} 0 & \text{for } -\infty \leq x \leq 0; \\ Ae^{-\alpha x} & \text{for } 0 \leq x \leq \infty. \end{cases}$$

¹Note: The initial position and momenta values could be fixed only within the limits imposed by uncertainty principle.

where $A, \alpha > 0$ are real constants that do not depend on x and t . Find A using the normalization condition.

Solution:

Computing the integral in eqn(2)

$$\int_{-\infty}^{\infty} dx |\psi(x, t)|^2 = A^2 \int_0^{\infty} dx e^{-2\alpha x} = A^2 \left. \frac{e^{-2\alpha x}}{-2\alpha} \right|_0^{\infty} = \frac{A^2}{2\alpha}$$

and equating it to unity we get,

$$A = \sqrt{2\alpha}.$$

Operators

Given the wavefunction we get the probability of finding the particle at a position. Can we get any more information about the particle from it? Values of all physical quantities related to the particle can be calculated using the wavefunction. These are the physical quantities that can be measured in experiments. The method to calculate these is to find the action of the *operator* corresponding to each physical quantity on the wavefunction. In these lectures, we will learn about only three physical quantities - position, momentum and energy. We will write down the operators corresponding to these and define how they act on the wavefunction.

$$\begin{aligned} \text{Position operator} & \quad \hat{x} \equiv x \\ \text{Momentum operator} & \quad \hat{p} \equiv -i\hbar \frac{\partial}{\partial x} \\ \text{Energy operator} & \quad \hat{E} \equiv i\hbar \frac{\partial}{\partial t} \end{aligned} \quad (3)$$

The action of these operators on the wavefunction are defined as

$$\hat{x}\psi(x, t) = x\psi(x, t) \quad (4)$$

$$\hat{p}\psi(x, t) = -i\hbar \frac{\partial \psi}{\partial x} \quad (5)$$

$$\hat{E}\psi(x, t) = i\hbar \frac{\partial \psi}{\partial t} \quad (6)$$

Eqn(4) defines the action of position operator \hat{x} on the wavefunction to be a multiplication with variable x . Similarly Eqn(5) (or Eqn(6)) defines the action of momentum (or energy) operator to be a multiplying with $-i\hbar$ (or $i\hbar$) the partial derivative of wavefunction with respect to position (or time).

If the action of the operator \hat{O} corresponding to some physical quantity on the wavefunction is such that it gives the same wavefunction multiplied by some constant, as given in

$$\hat{O}\psi^O(x, t) = \lambda_O \psi^O(x, t) \quad (7)$$

the constant λ_O is taken as the value of that physical quantity for the particle in the state $\psi(x, t)$. The constant λ is also called the *eigenvalue* of the operator \hat{O} . Wavefunctions that satisfy eqn(7) is called an *eigen wavefunction* of \hat{O} .

Example 2:

Let the wavefunction of a particle be $\psi^p(x, t) = C(t)e^{ikx}$. Where $C(t)$ is some function of time. Acting with momentum operator \hat{p} on this wavefunction

$$\hat{p}\psi(x, t) = -i\hbar \frac{\partial \psi}{\partial x} = (\hbar k)C(t)e^{ikx} = p \psi(x, t) \quad \text{where } p = \hbar k \text{ is the eigenvalue of momentum operator}$$

What does it physically mean if the state (or wavefunction) of the particle is an eigen wavefunction $\psi^O(x, t)$ of some operator \hat{O} ? In the experiment described above, if the several observers are measuring the value of the physical quantity represented by \hat{O} they will all find the value of the quantity to be λ_O .

However, if the action of operator \hat{O} on the wavefunction results in a function that is not a constant multiple of the wavefunction, we cannot find the precise value of the physical quantity. Nonetheless, we can find an *average value* of the quantity given by the expression

$$\langle \hat{O} \rangle = \int_{-\infty}^{\infty} dx \psi^*(x, t) \left(\hat{O}\psi(x, t) \right) \quad (8)$$

In eqn(8) above $\hat{O}\psi(x, t)$ inside the brackets indicates the action of operator \hat{O} on $\psi(x, t)$.

Example 3:

Let a particle be in a state represented by a wavefunction

$$\psi(x, t) = \begin{cases} 0 & \text{for } -\infty \leq x \leq 0; \\ \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) & \text{for } 0 \leq x \leq L \\ 0 & \text{for } L \leq x \leq \infty \end{cases}$$

Find the value of momentum for this particle.

Solution:

Acting with momentum operator on the given wavefunction

$$\hat{p}\psi(x, t) = -i\hbar \frac{\partial \psi}{\partial x} = \sqrt{\frac{2}{L}} \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right) \neq \lambda\psi(x, t)$$

Thus the given wavefunction is not an eigen wavefunction of momentum operator. We cannot find the precise value of momentum of the particle. We can only find the average value or expectation value of momentum given by

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} dx \psi^*(x, t) (\hat{p}\psi(x, t)) = \frac{2}{L} \frac{\pi}{L} \int_0^L dx \sin\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) = 0$$

Other physical quantities like angular momentum, kinetic energy etc. can also be calculated from the wavefunction using their respective operators in exactly the same fashion as described above.

Schrödinger's equation

How does the state of a particle change with time? If the state does change with time, the wavefunction of the particle must change accordingly. The change of wavefunction with time can be expressed in terms of the operators that we defined above. A large class of forces

experienced by a particle is only dependent on the position of the particle. There are several examples for this - gravitational force, electrostatic force and elastic restoring force are a few. The potential energy of the particle under such a force depends only on its position and one can write its total energy as

$$E = \text{K.E.} + \text{P.E.} = \frac{p^2}{2m} + V(x) \quad (9)$$

The expression in eqn(9) for energy holds true also as an operator equation. That is, if we treat the momentum and position on the RHS as operators, eqn(9) provides us an operator form of energy \hat{E} .

$$\hat{E} = \frac{\hat{p}^2}{2m} + V(\hat{x}) \quad (10)$$

We must be able to operate with the energy operator in eqn(10) on a wavefunction to find the energy of the particle as described above.

$$\hat{E}\psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi \quad (11)$$

In the above, we have used the operator form of \hat{p} and \hat{x} given in eqn(7). We can demand that the result of the above operation be equal to the one in eqn(6). Then we get

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi \quad (12)$$

Eqn(12) is called the Schrödinger's equation. Any wave function must obey this equation. This equation governs the change of the wavefunction with time. Notice that we have used the postulated form of the operators in eqns(4, 5, 6) to obtain this. It can be taken as a postulate inasmuch as Newton's law, that provides time rate of change of momentum to be force. Mathematically, Schrödinger equation is a second order partial differential equation.

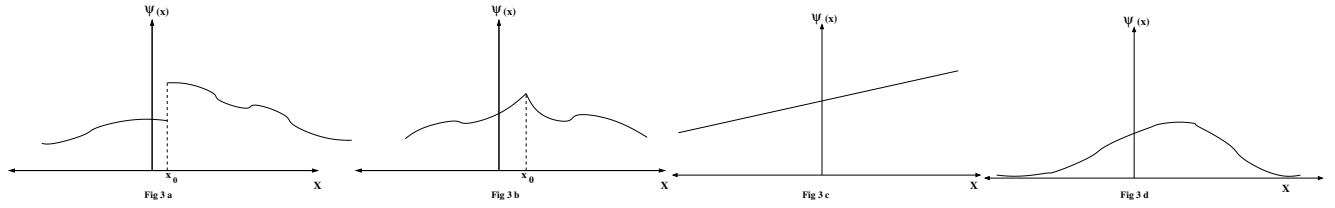
Conditions obeyed by wavefunction

Wavefunction will have to meet certain mathematical conditions if it has to obey the Schrödinger equation. Schrödinger equation has second order partial derivatives with respect to position variable x . If the potential $V(x)$ is a continuous and smooth (differentiable) function of position x , the wavefunction $\psi(x, t)$ will have to satisfy two conditions:

1. $\psi(x, t)$ must be a continuous function of x . and t .
2. $\frac{\psi(x, t)}{\partial x}$ must be a continuous function of x .
3. In addition, $\psi(x, t)$ must vanish for large values of position

$$\lim_{x \rightarrow \pm\infty} \psi(x, t) \rightarrow 0$$

The last condition arises because wavefunction must be always normalized as in eqn(2).



Example 4:

The function in fig(3a) above cannot be a wavefunction because it is discontinuous at $x = x_0$. The derivative of the function in fig(3b) is discontinuous at $x = x_1$ and makes this function unsuitable to be a wavefunction. The function in fig(3c) does not vanish for large values of x and thus cannot be a wavefunction. Fig(3d) shows a function that satisfies all the three properties that wavefunction need to obey.

Box normalization

Sometimes, the function we choose for the wavefunction do not meet the requirement 3 stated above. When such wavefunctions are substituted into the normalization condition eqn(2) we get infinity. Therefore we cannot use this wavefunction to describe the state of a particle, since it does not have a probability that adds up to 1. These are *non-normalizable* wavefunctions but we can create a normalizable wavefunction using the technique of box normalization. Let $\psi_{\text{non}}(x, t)$ be a non-normalizable wavefunction such that

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} dx |\psi_{\text{non}}(x, t)|^2 = A \quad (13)$$

where A is some finite real number, that usually depend on the length L of the interval. Then using $\psi_{\text{non}}(x, t)$, we can create a well behaved wavefunction $\psi_{\text{Box}}(x, t)$ as

$$\psi_{\text{Box}}(x, t) = \frac{1}{\sqrt{A}} \psi_{\text{non}}(x, t) \quad (14)$$

Such a wavefunction obeys the normalization condition even if we let the length of the interval $L \rightarrow \infty$.

$$\lim_{L \rightarrow \infty} \int_{-\frac{L}{2}}^{\frac{L}{2}} dx |\psi_{\text{Box}}(x, t)|^2 = \lim_{L \rightarrow \infty} \frac{1}{A} \int_{-\frac{L}{2}}^{\frac{L}{2}} dx |\psi_{\text{non}}(x, t)|^2 = \lim_{L \rightarrow \infty} \frac{1}{A} A = 1 \quad (15)$$

We can use $\psi_{\text{Box}}(x, t)$ as the wavefunction that describes a physical state of the particle.

Example 5:

Momentum eigen wavefunction $\psi_{\text{non}}(x, t) = e^{ikx}$ is non-normalizable as

$$\int_{-\infty}^{\infty} dx |\psi_{\text{non}}(x, t)|^2 = \int_{-\infty}^{\infty} dx |e^{ikx}|^2 = \int_{-\infty}^{\infty} dx 1 = \infty$$

Box normalized wavefunction for a particle in this state can be defined as

$$\psi_{\text{Box}}(x, t) = \frac{1}{\sqrt{L}} \psi_{\text{non}}(x, t)$$

Clearly

$$\lim_{L \rightarrow \infty} \int_{-\frac{L}{2}}^{\frac{L}{2}} dx |\psi_{\text{Box}}(x, t)|^2 = \lim_{L \rightarrow \infty} \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} dx 1 = 1$$

We can use $\psi_{\text{Box}}(x, t)$ as the wavefunction that correspond to a physical state of a free particle with definite value of momentum $p = \hbar k$.

Stationary states

Any wavefunction that describe a physical state of the particle must obey the Schrödinger equation (12). There is a special state of the particle with a definite value of the energy. The wavefunction $\psi^E(x, t)$ for this state will be an eigen wavefunction of the energy operator \hat{E} .

$$\hat{E}\psi^E(x, t) = i\hbar \frac{\partial \psi}{\partial t} = E\psi^E(x, t) \quad (16)$$

We choose a solution to the above equation of the form

$$\psi^E(x, t) = \psi^E(x, 0) e^{-\frac{iEt}{\hbar}} \quad (17)$$

where the function $\psi^E(x, 0)$ is the value of the eigen wavefunction at time $t = 0$, called stationary wavefunction. It is a function only of position and henceforth will be denote by just $\psi^E(x)$. By substituting eqn(17) into eqn(16) one can easily check that it is indeed a solution. The significance of the stationary wavefunction is that it determines the probability density at all times, that is,

$$|\psi^E(x, t)|^2 = |\psi^E(x)|^2 |e^{-\frac{iEt}{\hbar}}|^2 = |\psi^E(x)|^2$$

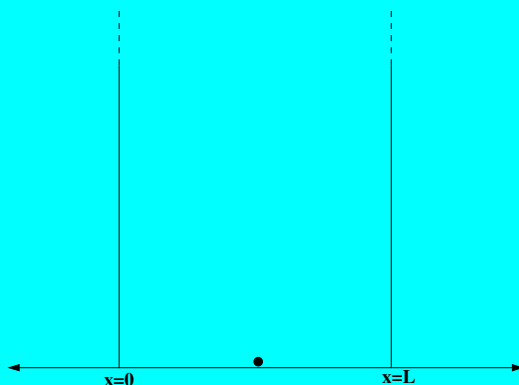
This means that if the particle is in a state with a definite value of energy, the probability density for finding it at a position is the same at any time. For this reason finding the stationary state for a particle becomes one of the most important tasks. In below we will find the probability density for a particle that is restricted to a region of length L , but is otherwise free.

Substituting eqn(17) into Schrödinger equation (12), we see that the oscillating time dependent phase $e^{-\frac{iEt}{\hbar}}$ cancels on both sides of the equation giving

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi^E}{\partial x^2} + V(x)\psi^E(x) = E\psi^E(x) \quad (18)$$

This equation is the *stationary Schrödinger equation*.

Particle in a box



Consider a particle which is restricted to a position interval $0 \leq x \leq L$, but is otherwise free to move. This amounts to putting the particle in a (one-dimensional) box that has walls of infinite height at $x = 0$ and $x = L$. A particle with finite energy can never escape this box as it requires infinite energy to jump out of the walls at $x = 0$ or $x = L$. In other words, any wavefunction for the particle must vanish outside the box.

$$\psi(x, t) = \begin{cases} 0 & \text{for } -\infty \leq x \leq 0; \\ 0 & \text{for } L \leq x \leq \infty \end{cases}$$

However, inside the box the wavefunction will be not be zero. We will now find the wavefunction that represents the particle with a definite value of energy E . This is just the eigen wavefunction of energy and we know that it must be in the form given in eqn(17), the only part we need to find is the stationary wavefunction $\psi^E(x)$. In below we will find this by solving the stationary Schrödinger equation (18) for this case.

Stationary Schrödinger equation for the particle in the region $0 < x < L$ is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi^E}{dx^2} = E\psi^E(x) \quad (19)$$

We obtained the above equation by putting $V(x) = 0$ in eqn(18) as the particle is free inside the box, with no potential energy. Since $\psi^E(x)$ is a function only of position x , its partial derivatives in eqn(18) are the same as total derivatives. Eqn(19) can be recast as

$$\frac{d^2\psi^E}{dx^2} = -\frac{2mE}{\hbar^2}\psi^E(x) \quad (20)$$

Solution ²to the above equation is standard, given by

$$\psi^E(x) = A \cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) + B \sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) \quad (21)$$

Note, the differential equation (20) is identical to the equation for a simple harmonic oscillator with angular frequency $\omega = \sqrt{\frac{2mE}{\hbar^2}}$. Here A and B are two constants, chosen to be real. To know the solution we must find the values of these constants. We will find these by using the

conditions discussed in the earlier section, that every wavefunction must obey. First of these conditions is that $\psi^E(x)$ must be continuous. If $\psi^E(x)$ has to be continuous at $x = 0$ then, as we approach the point $x = 0$ from the left of $x = 0$ or from right of $x = 0$, we must get the same value for the wavefunction. Towards the left of $x = 0$ is the region $-\infty \leq x \leq 0$ where the wavefunction is zero, as stated in the beginning of this section. Thus the wavefunction $\psi^E(x)$ inside the box must also vanish at $x = 0$, ie., $\psi^E(x = 0) = 0$. In eqn(21) if we put $x = 0$, we get

$$A = 0 \quad (22)$$

Using this back in eqn(21), we get

$$\psi^E(x) = B \sin \left(\sqrt{\frac{2mE}{\hbar^2}} x \right) \quad (23)$$

We find the constant B by using the normalization condition for $\psi^E(x, t)$

$$\begin{aligned} \int_0^L dx |\psi^E(x, t)|^2 &= \int_0^L dx |\psi^E(x)|^2 = 1 \\ \int_0^L dx |\psi^E(x)|^2 &= B^2 \int_0^L dx \sin^2 \left(\sqrt{\frac{2mE}{\hbar^2}} x \right) = B^2 \int_0^L dx \frac{1}{2} \\ &= \left(1 - \cos \left(\sqrt{\frac{2mE}{\hbar^2}} x \right) \right) = B^2 \frac{L}{2} \end{aligned} \quad (24)$$

This gives us the value for B as

$$B = \sqrt{\frac{L}{2}} \quad (25)$$

Substituting this value of B in eqn(23) we get

$$\psi^E(x) = \sqrt{\frac{2}{L}} \sin \left(\sqrt{\frac{2mE}{\hbar^2}} x \right) \quad (26)$$

Now we consider the point $x = L$. The above wavefunction must be continuous at $x = L$ also. Therefore when we approach the point $x = L$ from the left of $x = L$ or from right of $x = L$, we must get the same value for the wavefunction. Towards the right of $x = L$ is the region $L \leq x \leq \infty$ where the wavefunction is zero, as stated in the beginning of this section. Thus the wavefunction $\psi^E(x)$ inside the box must also vanish at $x = L$. If we put $x = L$ in eqn(26) we must get zero, ie., $\psi^E(x = L) = 0$. It is clear that this is possible only if

$$\sin \left(\sqrt{\frac{2mE}{\hbar^2}} L \right) = 0$$

We know that $\sin \theta$ vanishes if $\theta = n\pi$ for any integer value of n . Therefore the above condition can be satisfied if

$$\begin{aligned} \sqrt{\frac{2mE}{\hbar^2}} L &= n\pi \\ E &= \frac{n^2 \pi^2 \hbar^2}{2mL} \end{aligned}$$

where $n = 1, 2, 3, \dots$ (Here we exclude $n = 0$ since this would put the wavefunction to zero everywhere as that would be physically meaningless). From the above equation we find that the particle is allowed to have a discrete set of values of energy, usually denoted as

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL} \quad (27)$$

The wavefunction corresponding to this value of energy is

$$\psi^{E_n}(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (28)$$

The smallest energy possible for the particle in a box is $E_1 > 0$.