

PH 101: Physics I

Module 3: Introduction to Quantum Mechanics

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Recap

Schroedinger's equation and Wavefunction

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

- 1 Ψ must be continuous and single-valued everywhere.
- 2 $\partial \Psi / \partial x$, $\partial \Psi / \partial y$, $\partial \Psi / \partial z$ must be continuous and single-valued everywhere.
- 3 Ψ must be normalizable, which means that Ψ must go to 0 as $x \rightarrow \pm\infty$, $y \rightarrow \pm\infty$, $z \rightarrow \pm\infty$ in order that $\int |\Psi|^2 dV$ over all space be a finite constant.

Normalization:

The wavefunction Ψ satisfying the condition $\int_{-\infty}^{\infty} \Psi^* \Psi d^3r = 1$ is called normalised.

Operators: $\hat{O}\Psi = \Phi$

Any rule which changes one function

to other is called operation.

The representation of such a process is called the operator .

In quantum mechanics all physical quantities are

represented by linear operators

e.g. $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$, $\hat{E} = i\hbar \frac{\partial}{\partial t}$

Quantity	Operator
Position, x	x
Linear momentum, p	$\frac{\hbar}{i} \frac{\partial}{\partial x}$
Potential energy, $U(x)$	$U(x)$
Kinetic energy, $KE = \frac{p^2}{2m}$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Total energy, E	$i\hbar \frac{\partial}{\partial t}$
Total energy (Hamiltonian form), H	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x)$

Expectation value
of an operator

$$\langle G(x, p) \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{G} \Psi dx$$

Hermitian Operators and Eigen values

In quantum mechanics physical observables are represented by linear operators.

$$\langle Q \rangle = \int_{-\infty}^{\infty} \Psi^* Q \Psi d^3r$$

Since $\langle Q \rangle$ is a real quantity $\langle Q \rangle = \langle Q \rangle^*$

$$\text{But } \langle Q \rangle^* = \left(\int_{-\infty}^{\infty} \Psi^* Q \Psi d^3r \right)^* = \int_{-\infty}^{\infty} (Q\Psi)^* \Psi d^3r$$

$$\Rightarrow \int_{-\infty}^{\infty} \Psi^* Q \Psi d^3r = \int_{-\infty}^{\infty} (Q\Psi)^* \Psi d^3r$$

Operators satisfying this condition are called Hermitian operators

Exercise: Show Hermiticity of position and momentum operators.

Eigen Values: If operator operates on a function and gives some constant number times that function. The constant value is eigen value and that function is called eigen function that operator:

$$Q\Psi_q = q\Psi_q$$

Collection of all the eigenvalues of an operator Q is called its spectrum.

Observables in Quantum Mechanics: Eigen values

Example: Consider the function $f(x, t) = e^{i(kx - \omega t)}$.

This represents a wave travelling in x direction.

Operate on $f(x)$ with the momentum operator:

$$\begin{aligned}\hat{p}f(x) &= -i\hbar \frac{d}{dx} f(x) = (-i\hbar)(ik)e^{i(kx - \omega t)} \\ &= \hbar k f(x)\end{aligned}$$

since by the de Broglie relation $\hbar k$ is the momentum p of the particle.

$$\hat{p}f(x) = pf(x)$$

Observables in Quantum Mechanics: Hermitian operator

In quantum mechanics physical observables are represented by linear operators.

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Since $\langle Q \rangle$ is a real quantity $\langle Q \rangle = \langle Q \rangle^*$

$$\begin{aligned} \text{But } \langle Q \rangle^* &= \left(\int_{-\infty}^{\infty} \Psi^* Q \Psi d^3r \right)^* = \int_{-\infty}^{\infty} (Q\Psi)^* \Psi d^3r \\ &\Rightarrow \int_{-\infty}^{\infty} \Psi^* Q \Psi d^3r = \int_{-\infty}^{\infty} (Q\Psi)^* \Psi d^3r \end{aligned}$$

Examples:

(i) the operator \hat{x} is hermitian. Indeed:

$$\int (\hat{x}\psi)^* \psi dx = \int (x\psi)^* \psi dx = \int \psi^* x\psi dx = \int \psi^* \hat{x}\psi dx$$

(ii) the operator $\hat{p} = -i\hbar d/dx$ is hermitian:

$$\begin{aligned} \int (\hat{p}\psi)^* \psi dx &= \int \left(-i\hbar \frac{d\psi}{dx} \right)^* \psi dx \\ &= i\hbar \int \left(\frac{d\psi}{dx} \right)^* \psi dx \end{aligned}$$

and after integration by parts, and recognizing that the wfn tends to zero as $x \rightarrow \infty$, we get on the right-hand side

$$-i\hbar \int \psi^* \frac{d\psi}{dx} dx = \int \psi^* \hat{p}\psi dx$$

Time independent Schroedinger's equation

In a great many situations the potential energy of a particle does not depend on time explicitly; the forces that act on it, and hence U , vary with the position of the particle only. When this is true, Schrödinger's equation may be simplified by removing all reference to t .

Consider

$$\Psi = Ae^{-(i/\hbar)(Et - px)} = Ae^{-(iE/\hbar)t} e^{+(ip/\hbar)x} = \psi e^{-(iE/\hbar)t}$$

Substituting this in the Schroedinger's equation

$$E\psi e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m} e^{-(iE/\hbar)t} \frac{\partial^2 \psi}{\partial x^2} + U\psi e^{-(iE/\hbar)t}$$

Dividing through by the common exponential factor gives

Steady-state

**Schrödinger equation
in one dimension**

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - U)\psi = 0$$

**Hamiltonian
operator**

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U$$

and is called the **Hamiltonian operator** because it is reminiscent of the Hamiltonian function in advanced classical mechanics, which is an expression for the total energy of a system in terms of coordinates and momenta only. Evidently the steady-state Schrödinger equation can be written simply as

**Schrödinger's
equation**

$$\hat{H}\psi_n = E_n\psi_n$$

Time independent Schroedinger's equation

Steady-state
Schrödinger equation
in one dimension

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0$$

Note here that the function $\Psi(x, t)$ and $\psi(x)$ differ only by a time dependent phase factor of constant amplitude.

Therefore, $\psi(x)$ can be regarded as the time independent wave function.

$\Psi(x, t)$ is an eigen function of H with eigen value E and so is $\psi(x)$.

i.e. $\Psi(x, t)$ and $\psi(x)$ are states with definite energy.

These are called **stationary states** in quantum mechanics.

Solutions of Time independent Scrodinger Equation: Stationary states

Stationary states:

$$\Psi(r, t) = \psi(r) e^{-\frac{i}{\hbar} Et}$$

Properties:

(a) Stationary states are states with definite energy.

(b) Probability density of particles in the stationary states is independent of time.

$$P(x, t) = |\Psi(x, t)|^2 = \Psi^*(x, t) \Psi(x, t) = \psi(x) e^{\frac{i}{\hbar} Et} \psi^*(x) e^{-\frac{i}{\hbar} Et} = P(r)$$

(c) Expectation values observables or oparators representing physical quantities are independent of time.

$$\begin{aligned} \langle Q \rangle &= \frac{\int_{-\infty}^{\infty} \Psi^*(x, t) Q \Psi(x, t) dx}{\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx} \\ &= \frac{\int_{-\infty}^{\infty} \Psi^*(x) e^{\frac{i}{\hbar} Et} Q \Psi(x) e^{-\frac{i}{\hbar} Et} dx}{\int_{-\infty}^{\infty} \Psi^*(x) e^{\frac{i}{\hbar} Et} \Psi(x) e^{-\frac{i}{\hbar} Et} dx} \\ &= \frac{\int_{-\infty}^{\infty} \Psi^*(x) Q \Psi(x) dx}{\int_{-\infty}^{\infty} \Psi^*(x) \Psi(x) dx} \end{aligned}$$

Properties of Schroedinger's Equation

- (a) It is a single partial differential equation.
- (b) It is a first order in time derivative and second order in position.
- (c) Schroedinger's equation can not be derived from the first principle. It represents the first principle itself.
It can be regarded as a successful postulate just like Newton's second law in classical mechanics.
- (d) It is a linear equation as it does not contain higher powers of Ψ or its derivatives. (Important!!!)

Linearity property ensures that

- (i) If Ψ is the solution then a constant times Ψ is also a solution.
- (ii) If Ψ_1 and Ψ_2 are solutions then $c_1\Psi_1 + c_2\Psi_2$ is also a solution.

In general if $\Psi_1, \Psi_2, \Psi_3 \dots \Psi_n$ are solutions then a linear superposition or combination

$\Psi = \sum_n c_n \Psi_n$ is also a solution. (superposition principle).

Solution of the Schroedinger's equation

Basis states of the Hamiltonian: In the Schrodinger equation we encountered an

expression $\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t)\right)$. This is called the Hamiltonian operator or Hamiltonian for short. It acts on functions of x (and possibly t) and gives other functions as the end result. We denote the Hamiltonian by the symbol H .

$$H = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t)\right)$$

Consider the case when the potential energy is independent of time i.e. we write $V(x)$ instead of $V(x, t)$. Just as in rigid bodies, the moment of inertia matrix \mathbf{I} had specific directions e_1, e_2 and e_3 so that $\mathbf{I} e_j = I_j e_j$ called eigenvectors, we could also ask if there are special functions $\varphi_j(x)$ that have the eigenvector property.

$$H\varphi_j(x) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)\right)\varphi_j(x) = E_j \varphi_j(x)$$

Physical Interpretation of the complex matter wave

Then the functions $\varphi_j(x)$ would be analogous to finding the “principal directions” of the Hamiltonian. Just as in rigid bodies the three directions e_1, e_2 and e_3 were linearly independent and any other vector may be expressed as a linear combination of these directions viz. $v = \sum_j c_j e_j$ here too we may write for any function $\psi(x, t)$,

$$\psi(x, t) = \sum_j c_j(t) \varphi_j(x)$$

Physical Interpretation of the complex matter wave

Specifically we want $\psi(x, t)$ to obey Schrodinger's equation. This means,

$$i \hbar \frac{\partial}{\partial t} \psi(x, t) = \sum_j i \hbar \frac{d}{dt} c_j(t) \varphi_j(x) \text{ and } \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right) \psi(x, t) = \sum_j E_j c_j(t) \varphi_j(x)$$

or,

$$i \hbar \frac{d}{dt} c_j(t) = E_j c_j(t) \text{ which means } c_j(t) = e^{-\frac{i}{\hbar} E_j t} c_j(0)$$

If we assume that $c_j(0) = 0$ for all j except one special $j = n$ where $c_n(0) = 1$ then we obtain a stationary state.

$$\psi(x, t) = e^{-\frac{i}{\hbar} E_n t} \varphi_n(x)$$

This has the property that the probability density $|\psi(x, t)|^2$ is independent of time. It also means all expectation values are independent of time.

$$\langle A \rangle = \int dx \psi^*(x, t) A \psi(x, t) = \int dx \varphi_n^*(x) A \varphi_n(x)$$

Application

In this part we will try to understand some of the interesting application of the **Schroedinger's Equation**.

Goal is to

- (a) Write down the Schroedinger's equation given the potential energy.
- (b) Solve the Schroedinger's equation using the properties of the wave function (the boundary conditions).
- (c) Obtain the energy eigenvalues(spectrum) and eigen functions.
- (d) Obtain the wave function.

Examples:

- 1) Particle in a box.
- 2) Finite square well potential.
- 3) Harmonic oscillator.

Initial and boundary conditions in quantum physics

In quantum physics, as we know very well by now, there is nothing like a trajectory - so that it is not Newton's Second Law that we should be integrating, but Schrodinger's matter wave equation. This as we know may be written as,

$$i \hbar \frac{\partial}{\partial t} \psi(x, t) = \left(- \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right) \psi(x, t) \dots\dots\dots(1)$$

This is an equation with two x derivatives and one t derivative. This is called a partial differential equation. Fixing the boundary conditions on this somewhat more technical so let us focus on the simpler case of stationary states. In case of stationary states $V(x)$ is independent of time so that,

$$\psi(x, t) = e^{-\frac{i}{\hbar} E t} \varphi(x)$$

Substituting into (1) gives us the so-called time independent Schrodinger equation -

$$\left(- \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \varphi(x) = E \varphi(x)$$

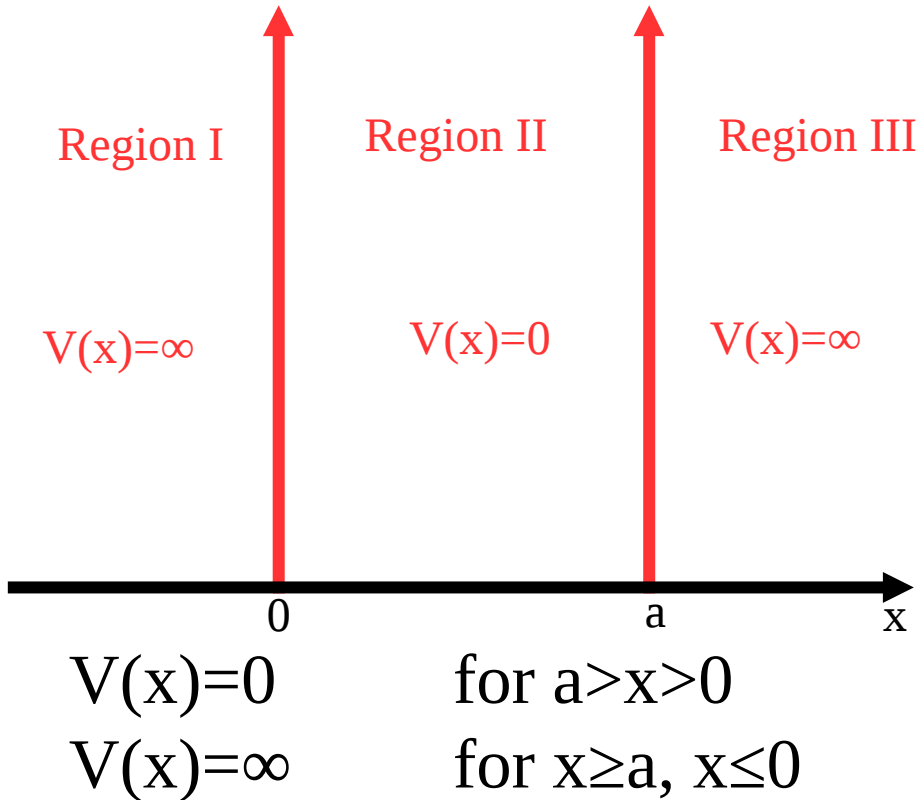
Time Independent Schrodinger Equation

Now this is somewhat like our Newton's second law which has two derivatives with respect to one independent variable. As before, integrating this twice will give us $\varphi(x)$. But each time an integration is performed, we have to introduce an integration constant. To get rid of the two integration constants and write down a unique solution, we have to **specify $\varphi(x_0)$ and $\varphi'(x_0)$** . **This is known as specifying boundary conditions** (if time is the independent variable, it is called initial condition). This is fully analogous to the case in Newtonian mechanics where we have to specify $x(t_0)$ and $x'(t_0) \equiv v(t_0)$.

Also, keep in mind that Schrodinger's equation is a homogeneous equation – this means that if $\psi(x, t)$ is a solution then $\lambda \psi(x, t)$ is also a solution where λ is any complex constant. This also applies to the time independent equation – if $\varphi(x)$ is a solution then $\lambda \varphi(x)$ is also a solution where λ is any complex constant. This ambiguity is removed by imposing **the normalization condition**, i.e. by applying the condition that the total probability of finding the particle somewhere in space is one.

$$\text{Normalization condition: } \int_{-\infty}^{\infty} dx |\varphi(x)|^2 = 1$$

Particle in one-dimension box



Classical Physics: The particle can exist anywhere in the box and follow a path in accordance to Newton's Laws.

Quantum Physics: The particle is expressed by a wave function and there are certain areas more likely to contain the particle within the box.

Time Dependent Schrödinger Equation

$$\underbrace{-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2}}_{\text{KE}} + \underbrace{V(x)\Psi}_{\text{PE}} = \underbrace{E\Psi}_{\text{TE}}$$

Wave function is dependent on time and position function:

$$\psi(x, t) = e^{iEt/\hbar} \psi(x)$$

Time Independent Schrödinger Equation

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

Applying boundary conditions:

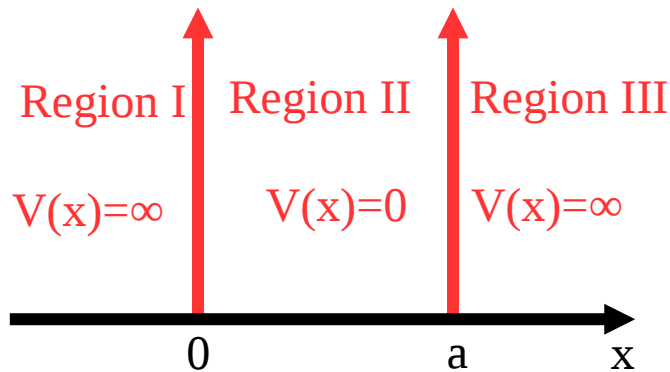
Region I and III:

$$|\psi|^2 = 0$$

Region II:

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

Particle in one-dimension box



Region I and III:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \infty \psi = E\psi \longrightarrow |\psi|^2 = 0$$

Region II: $\frac{d^2\psi}{dx^2} = -k^2\psi$ where, $k = \frac{\sqrt{2mE}}{\hbar}$

The equation is similar to **simple harmonic oscillator**. The solution is thus of the form

$$\psi(x) = A \sin kx + B \cos kx,$$

where A and B are arbitrary constants fixed by the **boundary conditions** of the problem.

Boundary Condition is that the wave function is continuous, i.e.,

$$\psi(0) = \psi(a) = 0$$

$$\psi(0) = A \sin 0 + B \cos 0 = 0 \implies B = 0$$

and hence, $\psi(x) = A \sin kx$.

$$\psi(a) = A \sin ka = 0$$

either $A = 0$ or $\sin ka = 0$ (**$A = 0$, trivial solution**)

$ka = 0, \pm\pi, \pm2\pi, \pm3\pi, \dots$ (**$k = 0$, trivial solution**)

$$k_n = \frac{n\pi}{a}, \text{ with } n = 1, 2, 3, \dots$$

Particle in one-dimension box

$$k_n = \frac{n\pi}{a}, \text{ with } n = 1, 2, 3, \dots$$

So, the energy of such a particle in the box is given by

Energy:
$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}.$$

To find A , we normalize ψ

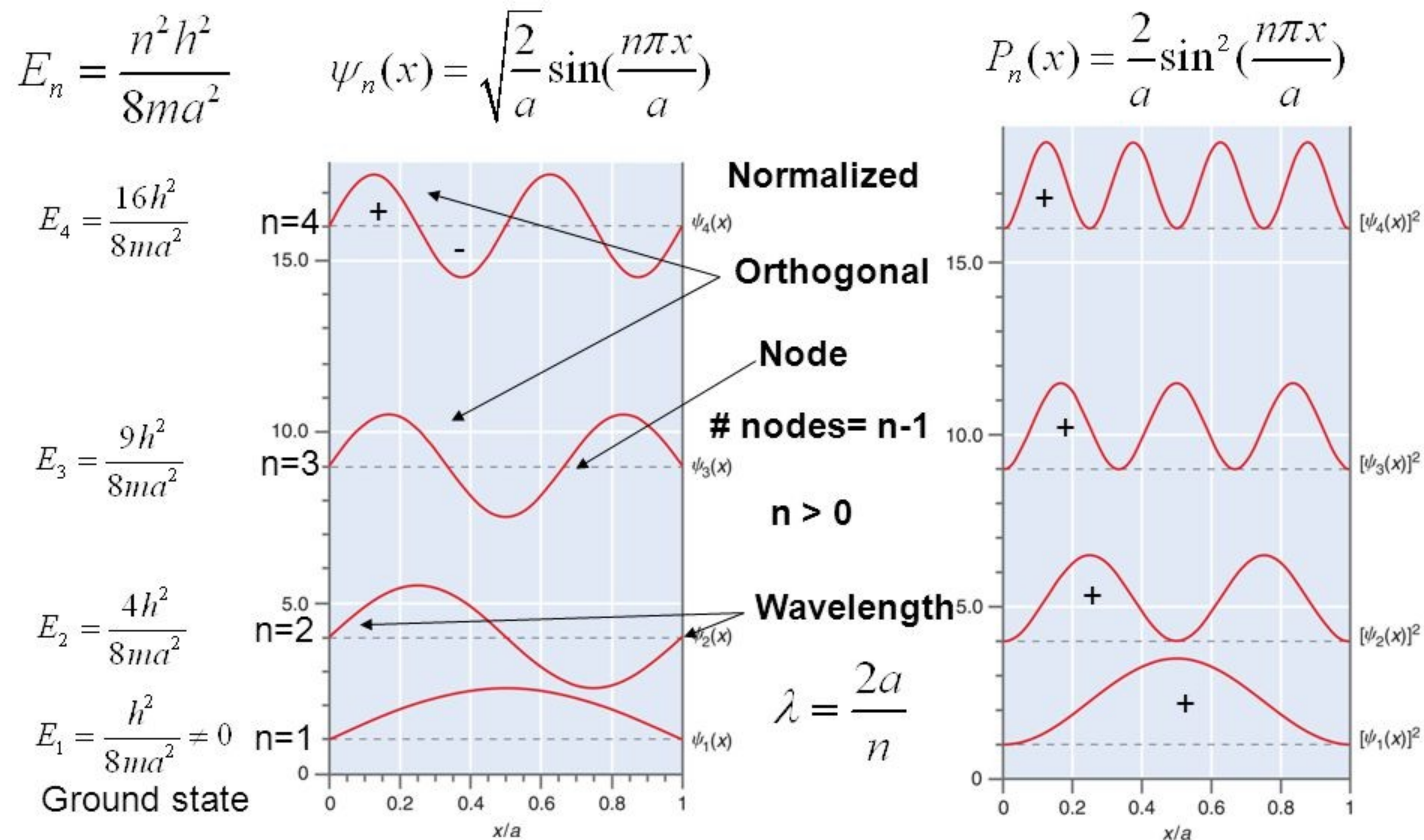
$$\int_0^a |A|^2 \sin^2(kx) dx = |A|^2 \frac{a}{2} = 1, \text{ so } |A|^2 = \frac{2}{a}$$

Inside the well, the solutions are (the phase of A carries no physical significance, hence is taken as positive)

Wavefunction:
$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

Time independent Schroedinger equation has an infinite set of solution (one for each positive n).

Particle in a Box Wavefunctions



Important properties of the wave function:

1. They are alternately even and odd, with respect to the center of the well: ψ_1 is even, ψ_2 is odd, ψ_3 is even, and so on.
2. As you go up in energy, each successive state has one more node (zero-crossing): ψ_1 has none (the end points don't count), ψ_2 has one, ψ_3 has two, and so on.
3. They are mutually orthogonal, in the sense that $\int \psi_m(x)^* \psi_n(x) dx = 0$, whenever $m \neq n$.

Position and Momentum

Position:

$$\begin{aligned}\langle x \rangle &= \int_{-\infty}^{\infty} x |\psi|^2 dx = \frac{2}{L} \int_0^L x \sin^2 \frac{n\pi x}{L} dx \\ &= \frac{2}{L} \left[\frac{x^2}{4} - \frac{x \sin(2n\pi x/L)}{4n\pi/L} - \frac{\cos(2n\pi x/L)}{8(n\pi/L)^2} \right]_0^L\end{aligned}$$

Since $\sin n\pi = 0$, $\cos 2n\pi = 1$, and $\cos 0 = 1$, for all the values of n the expectation value of x is

$$\langle x \rangle = \frac{2}{L} \left(\frac{L^2}{4} \right) = \frac{L}{2}$$

This result means that the average position of the particle is the middle of the box in all quantum states. There is no conflict with the fact that $|\psi|^2 = 0$ at $L/2$ in the $n = 2, 4, 6, \dots$ states because $\langle x \rangle$ is an *average*, not a probability, and it reflects the symmetry of $|\psi|^2$ about the middle of the box.

Position and Momentum

Momentum:

$$\begin{aligned}\langle p \rangle &= \int_{-\infty}^{\infty} \psi^* \hat{p} \psi \, dx = \int_{-\infty}^{\infty} \psi^* \left(\frac{\hbar}{i} \frac{d}{dx} \right) \psi \, dx \\ &= \frac{\hbar}{i} \frac{2}{L} \frac{n\pi}{L} \int_0^L \sin \frac{n\pi x}{L} \cos \frac{n\pi x}{L} \, dx\end{aligned}$$

note that $\int \sin ax \cos ax \, dx = \frac{1}{2a} \sin^2 ax$

With $a = n\pi/L$ we have

$$\langle p \rangle = \frac{\hbar}{iL} \left[\sin^2 \frac{n\pi x}{L} \right]_0^L = 0$$

since $\sin^2 0 = \sin^2 n\pi = 0 \quad n = 1, 2, 3, \dots$

This is strange!!!

$$p_n = \pm \sqrt{2mE_n} = \pm \frac{n\pi\hbar}{L} \quad p_{\text{av}} = \frac{(+n\pi\hbar/L) + (-n\pi\hbar/L)}{2} = 0$$

Physical Interpretation of the complex matter wave

Q. A stationary state of a quantum particle has an eigen function described by,

$$\varphi_0(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) ; & 0 < x < L \\ 0 ; & \text{otherwise} \end{cases}$$

a) Find the expectation value of the position.

$$\langle x \rangle = \int_0^L \varphi_0(x) x \varphi_0(x) dx = \frac{L}{2}$$

b) Find the expectation value of the momentum.

$$\langle p \rangle = \int_0^L \varphi_0(x) \left(-i \hbar \frac{\partial}{\partial x}\right) \varphi_0(x) dx = 0$$

This is because the waves are moving in both directions.

c) Find the expectation value of the kinetic energy.

$$\langle KE \rangle = \frac{1}{2m} \int_0^L \varphi_0(x) \left(-i \hbar \frac{\partial}{\partial x} \right)^2 \varphi_0(x) dx = \frac{\hbar^2 \pi^2}{2m L^2}$$

d) Find the probability that the particle is between 0 and L/4

$$\text{probability} = \int_0^{L/4} \varphi_0(x) \varphi_0(x) dx = \frac{\pi-2}{(4 \pi)} = 0.09$$

e) Estimate the size of the deviation of the position of the particle from its expected value.

$$\text{Deviation from expected value} = x - \frac{L}{2}$$

But is as likely for the particle to be to the left of $x = \frac{L}{2}$ as it is to the right of this value.

We want to know how far in absolute terms it can be found far away from $x = \frac{L}{2}$. For this we can do one of two things. We could calculate the average of $|x - \frac{L}{2}|$. This means we could say,

$$\Delta x = \int_0^L \varphi_0(x) |x - \frac{L}{2}| \varphi_0(x) dx$$

which is possible but the absolute value is a mathematically clumsy operation since we have to take into account the cases $x > \frac{L}{2}$ and $x < \frac{L}{2}$ separately while performing the above integral [do it as a homework]. What is usually done is to find the average of the square of $x - \frac{L}{2}$ and then we get a quantity whose units is $[\text{length}]^2$ but represents the deviation from the average value. To get a quantity with units of length we simply take the square root at the end. This is called RMS value.

$$(\Delta x)^2 = \int_0^L \varphi_0(x) \left(x - \frac{L}{2}\right)^2 \varphi_0(x) dx$$

In the present example we may evaluate this to get, $\Delta x = \mathbf{0.18 L}$. Hence the quantum particle is most likely to be found between $0.5 L - 0.18 L$ and $0.5 L + 0.18 L$.

Next natural question is how likely is most likely? The probability that the particle is found between $0.5 L - 0.18 L$ and $0.5 L + 0.18 L$ is,

$$\text{probability} = \int_{0.5 L - 0.18 L}^{0.5 L + 0.18 L} \varphi_0(x) \varphi_0(x) dx = 0.65$$

or 65% probability. If you want a higher probability choose, the interval to be $\frac{L}{2} - 2 \Delta x$ and $\frac{L}{2} + 2 \Delta x$. The probability that the particle is in this interval now is much higher.

$$\text{probability} = \int_{0.5 L - 0.36 L}^{0.5 L + 0.36 L} \varphi_0(x) \varphi_0(x) dx = 0.97$$

or 97% probability.

e) Estimate the size of the deviation of the momentum of the particle from its expected value.

This is easier to do since the expected value of momentum is zero.

$$(\Delta p)^2 = \int_0^L \varphi_0(x) \left(-i \hbar \frac{\partial}{\partial x} - 0 \right)^2 \varphi_0(x) dx = \langle p^2 \rangle = 2m \langle KE \rangle = \frac{\hbar^2 \pi^2}{L^2}$$

or $\Delta \mathbf{p} = \frac{\hbar \pi}{L}$ Combining with the earlier result namely, $\Delta \mathbf{x} = \mathbf{0.18 L}$ we conclude that

$$\Delta x \Delta \mathbf{p} = \mathbf{0.565 \hbar} > \hbar/2$$

which is consistent with **Heisenberg's uncertainty principle**.