The probability per unit volume of finding a photon somewhere is proportional to the number of photons per unit volume there:

\[
\frac{P}{V} \propto \frac{N}{V}
\]

\[
\frac{N}{V} \propto I
\]

\[
I \propto E^2
\]

\[
\frac{P}{V} \propto E^2
\]

The probability per unit volume of finding a photon is proportional to the square of the amplitude of the associated e/m wave.

Since all forms of matter show wave-particle duality we can apply this idea to other particles too:

**The probability per unit volume of finding a particle somewhere is proportional to the square of the amplitude of the associated de Broglie wave.**

Amplitude of the associated wave is called the **probability amplitude** or the **Wave function** \((\Psi)\)

For example, the wave function for a free particle with a precisely known momentum \(p_x\):

\[
\Psi(x,t) = A \cos(kx - \omega t)
\]

\[
\Psi(x,t) = A[\cos(kx - \omega t) + i \sin(kx - \omega t)]
\]

\[
= Ae^{i(kx-\omega t)}
\]

\[
= Ae^{ikx} e^{-i\omega t}
\]

\[
= A \psi(x) e^{-i\omega t}
\]

If the potential energy of the system does not vary with time, the time and spatial dependences of the wave function can be separated; and the time dependence can be represented simply by \(e^{-i\omega t}\) as in this case, so we will concentrate only on the space part: \(\psi(x)\)

Since the wave function is often complex valued:

\[
|\psi|^2 = \psi^* \psi
\]
The probability of finding the particle in a volume $dV$: $|\psi|^2 dV$

We will deal only with one-dimensional systems where the particle must be located along the $x$ axis. So the probability of finding the particle in an interval $dx$: $|\psi|^2 dx$

the probability of finding the particle in the interval between $a$ and $b$: $P_{ab} = \int_a^b |\psi|^2 dx$

Since the particle must be found somewhere along the $x$ axis: $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$

When this condition is satisfied the wave function is said to be normalized.

$\psi(x)$ must be continuous in space with no discontinuous jumps

$\psi(x)$ must be defined at all points in space and be single –valued.

The average values of parameters like the position ($x$), momentum ($p$) and energy ($E$) can be extracted out from the wave function. These average values are called the expectation values of the variables:

The average position, or the expectation value of $x$ is defined by the equation:

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* x \psi \, dx$$

Brackets $\langle \rangle$ denote the expectation value

The expectation value for any function $f(x)$ (like energy) associated with the particle is given by the equation:

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} \psi^* f(x) \psi \, dx$$
Example: A particle in a box: consider a particle trapped in a 1D-box bouncing back and forth between the walls. Since there is zero probability of finding the particle outside, \( \psi(x)=0 \) outside the box; and since the wave-function must be continuous, \( \psi(x)=0 \) at the walls too.

\[
\psi(x) = A \sin kx + B \cos kx
\]

\[
\psi(0) = A \sin 0 + B \cos 0 = B
\]

\[
\psi(L) = A \sin kL = 0
\]

\[
kL = n\pi
\]

\[
\frac{\sqrt{2mE}}{\hbar} L = n\pi
\]

\[
E_n = \left( \frac{\hbar^2}{8mL^2} \right) n^2
\]

\[
\psi(x) = A \sin \left( \frac{n\pi x}{L} \right)
\]

The quantization of energy comes out naturally from quantum mechanics and is not an ad-hoc concept as was the case in Planck’s theory.

Normalization requires

\[
\int_{\text{all space}} |\psi|^2 \, dx = 1
\]

\[
\int_0^L A^2 \sin^2 \left( \frac{n\pi x}{L} \right) \, dx = A^2 \left( \frac{L}{2} \right) = 1
\]

or

\[
A = \sqrt{\frac{2}{L}}
\]

\[
\psi(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right)
\]

\[
\lambda_n = \frac{2L}{n}
\]
Consider \( \psi(x) = A \sin(kx) \)

\[
\frac{d}{dx} A \sin(kx) = A k \cos(kx) \quad \text{and} \quad \frac{d^2}{dx^2} \psi = -A k^2 \sin(kx)
\]

But: the kinetic energy: \( K = \frac{p^2}{2m} \), and \( k = \frac{p}{\hbar} \)

\[
-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + \frac{\hbar^2 k^2}{2m} A \sin(kx) = \frac{\hbar^2}{4\pi^2(\lambda^2)(2m)} \psi = \frac{p^2}{2m} \psi = \frac{m^2 \nu^2}{2m} \psi = \frac{1}{2} m \nu^2 \psi = K \psi
\]

Energy conservation:

\[
K + U = E
\]

\[
(K + U)\psi = E\psi
\]

\[
K\psi + U\psi = E\psi
\]

\[
-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + U\psi = E\psi
\]

**Schroedinger Equation**: The basic wave equation of non-relativistic Quantum Mechanics
Examples:

1. A proton is confined to move in a one-dimensional box of length 0.200 nm. (a) Find the lowest possible energy of the proton. (b) What If? What is the lowest possible energy of an electron confined to the same box? (c) How do you account for the great difference in your results for (a) and (b)?

The ground state energy of a particle (mass m) in a 1-dimensional box of width \( L \) is \( E_1 = \frac{\hbar^2}{8mL^2} \).

(a) For a proton \( m = 1.67 \times 10^{-27} \text{ kg} \) in a 0.200-nm wide box:

\[
E_1 = \frac{\left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right)^2}{8\left(1.67 \times 10^{-27} \text{ kg}\right)\left(2.00 \times 10^{-10} \text{ m}\right)^2} = 8.22 \times 10^{-22} \text{ J} = 5.13 \times 10^{-19} \text{ eV}.
\]

(b) For an electron \( m = 9.11 \times 10^{-31} \text{ kg} \) in the same size box:

\[
E_1 = \frac{\left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right)^2}{8\left(9.11 \times 10^{-31} \text{ kg}\right)\left(2.00 \times 10^{-10} \text{ m}\right)^2} = 1.51 \times 10^{-18} \text{ J} = 9.41 \text{ eV}.
\]

(c) The electron has a much higher energy because it is much less massive.

2. A particle in an infinitely deep square well has a wave function given by

\[
\psi_2(x) = \frac{2}{L} \sin \left(\frac{2\pi x}{L}\right)
\]

for \( 0 \leq x \leq L \) and zero otherwise.

(a) Determine the expectation value of \( x \).

(b) Determine the probability of finding the particle near \( L/2 \), by calculating the probability that the particle lies in the range \( 0.490L \leq x \leq 0.510L \).

(c) What If? Determine the probability of finding the particle near \( L/4 \), by calculating the probability that the particle lies in the range \( 0.240L \leq x \leq 0.260L \).

(d) Argue that the result of part (a) does not contradict the results of parts (b) and (c).
(a) \[ \langle x \rangle = \frac{L}{2} \left[ \frac{2}{L} \sin \left( \frac{2\pi x}{L} \right) \right] dx - \frac{2I}{L} \left[ \frac{1}{2} - \frac{L}{4\pi} \cos \frac{4\pi x}{L} \right] \]

\[ \langle x \rangle = \frac{1}{L} \left( \frac{L^2}{2} - \frac{1}{L} \frac{L^2}{2} \right) = \frac{L}{2} \]

(b) Probability \[ = \int_{0.06L}^{0.51L} \frac{2}{L} \sin \left( \frac{2\pi x}{L} \right) \] dx

\[ = \left[ \frac{1}{L} - \frac{L}{4\pi} \sin \frac{4\pi x}{L} \right]_{0.06L}^{0.51L} \]

\[ = 0.020 - \frac{L}{4\pi} (\sin 2.04\pi - \sin 1.96\pi) = 3.26 \times 10^{-3} \]

(c) Probability \[ \left[ \frac{x}{L} - \frac{1}{4\pi} \sin \frac{4\pi x}{L} \right] \]

\[ = 3.99 \times 10^{-2} \]

(d) In the n = 2 graph in Figure 41.4 (b), it is more probable to find the particle either near \( x = \frac{L}{4} \) or \( x = \frac{3L}{4} \) than at the center, where the probability density is zero.

Nevertheless, the symmetry of the distribution means that the average position is \( \frac{L}{2} \).