Schrödinger's Equation

Consider a dynamical system consisting of a single non-relativistic particle of mass m moving along the x-axis in some real potential $V(x)$. In quantum mechanics, the instantaneous state of the system is represented by a complex wavefunction $\psi(x,t)$. This wavefunction evolves in time according to Schrödinger's equation:

$$\mathrm{i}\,\hbar\,\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2\,m}\frac{\partial^2\psi}{\partial x^2} + V(x)\,\psi. \tag{137}$$

The wavefunction is interpreted as follows: $|\psi(x,t)|^{\,2}$ is the probability density of a measurement of the particle's displacement yielding the value x. Thus, the probability of a measurement of the displacement giving a result between a and b (where $a < b$) is

$$P_{x\,\in\,a:b}(t) = \int_a^b |\psi(x,t)|^{\,2}\,dx. \tag{138}$$

Note that this quantity is real and positive definite.

Normalization of the Wavefunction

Now, a probability is a real number between 0 and 1. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. According to Eq. (138), the probability of a measurement of x yielding a result between $-\infty$ and $+\infty$ is

$$P_{x\,\in\,-\infty:\infty}(t) = \int_{-\infty}^{\infty} |\psi(x,t)|^{\,2}\,dx. \tag{139}$$

However, a measurement of x *must* yield a value between $-\infty$ and $+\infty$, since the particle has to be located somewhere. It follows that $P_{x\,\in\,-\infty:\infty} = 1$, or

$$\int_{-\infty}^{\infty} |\psi(x,t)|^{\,2}\,dx = 1, \tag{140}$$

which is generally known as the *normalization condition* for the wavefunction.

For example, suppose that we wish to normalize the wavefunction of a Gaussian wave packet, centered on $x = x_0$, and of characteristic width σ

$$\psi(x) = \psi_0\, \mathrm{e}^{-(x-x_0)^2/(4\sigma^2)}. \tag{141}$$

In order to determine the normalization constant ψ_0, we simply substitute Eq. (141) into Eq. (140), to obtain

$$|\psi_0|^2 \int_{-\infty}^{\infty} \mathrm{e}^{-(x-x_0)^2/(2\sigma^2)}\, dx = 1. \tag{142}$$

Changing the variable of integration to $y = (x - x_0)/(\sqrt{2}\,\sigma)$, we get

$$|\psi_0|^2 \sqrt{2}\,\sigma \int_{-\infty}^{\infty} \mathrm{e}^{-y^2}\, dy = 1. \tag{143}$$

However,

$$\int_{-\infty}^{\infty} \mathrm{e}^{-y^2}\, dy = \sqrt{\pi}, \tag{144}$$

which implies that

$$|\psi_0|^2 = \frac{1}{(2\pi\,\sigma^2)^{1/2}}. \tag{145}$$

Hence, a general normalized Gaussian wavefunction takes the form

$$\psi(x) = \frac{e^{i\,\varphi}}{(2\pi\,\sigma^2)^{1/4}}\,e^{-(x-x_0)^2/(4\sigma^2)}, \tag{146}$$

where φ is an arbitrary real phase-angle.

Now, it is important to demonstrate that if a wavefunction is initially normalized then it stays normalized as it evolves in time according to Schrödinger's equation. If this is not the case then the probability interpretation of the wavefunction is untenable, since it does not make sense for the probability that a measurement of x yields *any* possible outcome (which is, manifestly, unity) to change in time. Hence, we require that

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi(x,t)|^2\,dx = 0, \tag{147}$$

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi(x,t)|^2\,dx = 0,$$

for wavefunctions satisfying Schrödinger's equation. The above equation gives

$$\frac{d}{dt}\int_{-\infty}^{\infty}\psi^*\,\psi\,dx = \int_{-\infty}^{\infty}\left(\frac{\partial\psi^*}{\partial t}\,\psi + \psi^*\,\frac{\partial\psi}{\partial t}\right)dx = 0.$$

Now, multiplying Schrödinger's equation by $\psi^*/(\mathrm{i}\,\hbar)$, we obtain

$$\psi^*\,\frac{\partial\psi}{\partial t} = \frac{\mathrm{i}\,\hbar}{2\,m}\,\psi^*\,\frac{\partial^2\psi}{\partial x^2} - \frac{\mathrm{i}}{\hbar}\,V\,|\psi|^2.$$

The complex conjugate of this expression yields

$$\psi\,\frac{\partial\psi^*}{\partial t} = -\frac{\mathrm{i}\,\hbar}{2\,m}\,\psi\,\frac{\partial^2\psi^*}{\partial x^2} + \frac{\mathrm{i}}{\hbar}\,V\,|\psi|^2$$

[since $(A\,B)^* = A^*\,B^*$, $A^{**} = A$, and $i^* = -i$]. Summing the previous two equations, we get

$$\frac{\partial\psi^*}{\partial t}\,\psi+\psi^*\,\frac{\partial\psi}{\partial t} = \frac{\mathrm{i}\,\hbar}{2\,m}\left(\psi^*\,\frac{\partial^2\psi}{\partial x^2} - \psi\,\frac{\partial^2\psi^*}{\partial x^2}\right) = \frac{\mathrm{i}\,\hbar}{2\,m}\,\frac{\partial}{\partial x}\left(\psi^*\,\frac{\partial\psi}{\partial x} - \psi\,\frac{\partial\psi^*}{\partial x}\right). \tag{151}$$

Equations (148) and (151) can be combined to produce

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2\,dx = \frac{\mathrm{i}\,\hbar}{2m}\left[\psi^*\,\frac{\partial\psi}{\partial x} - \psi\,\frac{\partial\psi^*}{\partial x}\right]_{-\infty}^{\infty} = 0. \tag{152}$$

The above equation is satisfied provided

$$|\psi| \rightarrow 0 \quad \text{as} \quad |x| \rightarrow \infty. \tag{153}$$

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2\,dx = \frac{\mathrm{i}\,\hbar}{2\,m}\left[\psi^*\,\frac{\partial\psi}{\partial x} - \psi\,\frac{\partial\psi^*}{\partial x}\right]_{-\infty}^{\infty} = 0. \tag{152}$$

The above equation is satisfied provided

$$|\psi| \rightarrow 0 \quad \text{as} \quad |x| \rightarrow \infty. \tag{153}$$

However, this is a necessary condition for the integral on the left-hand side of Eq. (140) to converge. Hence, we conclude that all wavefunctions which are *square-integrable* [*i.e.*, are such that the integral in Eq. (140) converges] have the property that if the normalization condition (140) is satisfied at one instant in time then it is satisfied at all subsequent times.

It is also possible to demonstrate, via very similar analysis to the above, that

$$\frac{dP_{x\,\in\,a:b}}{dt} + j(b,t) - j(a,t) = 0, \tag{154}$$

where $P_{x\,\in\,a:b}$ is defined in Eq. (138), and

$$j(x,t) = \frac{\mathrm{i}\,\hbar}{2\,m}\left(\psi\,\frac{\partial\psi^*}{\partial x} - \psi^*\,\frac{\partial\psi}{\partial x}\right) \tag{155}$$

$$\frac{dP_{x\in a:b}}{dt} + j(b,t) - j(a,t) = 0, \tag{154}$$

where $P_{x\in a:b}$ is defined in Eq. (138), and

$$j(x,t) = \frac{\mathrm{i}\,\hbar}{2\,m}\left(\psi\,\frac{\partial\psi^*}{\partial x} - \psi^*\,\frac{\partial\psi}{\partial x}\right) \tag{155}$$

is known as the *probability current*. Note that j is real. Equation (154) is a *probability conservation equation*. According to this equation, the probability of a measurement of x lying in the interval a to b evolves in time due to the difference between the flux of probability into the interval [*i.e.*, $j(a,t)$], and that out of the interval [*i.e.*, $j(b,t)$]. Here, we are interpreting $j(x,t)$ as the *flux* of probability in the $+x$-direction at position x and time t.

Note, finally, that not all wavefunctions can be normalized according to the scheme set out in Eq. (140). For instance, a plane wave wavefunction

$$\psi(x,t) = \psi_0\,{\rm e}^{\,{\rm i}\,(k\,x-\omega\,t)} \tag{156}$$

is not square-integrable, and, thus, cannot be normalized. For such wavefunctions, the best we can say is that

$$P_{x\,\in\,a:b}(t) \propto \int_a^b |\psi(x,t)|^{\,2}\,dx. \tag{157}$$

In the following, all wavefunctions are assumed to be square-integrable and normalized, unless otherwise stated.

Expectation Values and Variances

We have seen that $|\psi(x,t)|^2$ is the probability density of a measurement of a particle's displacement yielding the value x at time t. Suppose that we made a large number of independent measurements of the displacement on an equally large number of identical quantum systems. In general, measurements made on different systems will yield different results. However, from the definition of probability, the mean of all these results is simply

$$\langle x\rangle = \int_{-\infty}^{\infty} x\,|\psi|^2\,dx. \tag{158}$$

Here, $\langle x\rangle$ is called the *expectation value* of x. Similarly the expectation value of any function of x is

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)\,|\psi|^2\,dx. \tag{159}$$

In general, the results of the various different measurements of x will be scattered around the expectation value $\langle x\rangle$. The degree of scatter is parameterized by the quantity

$$\sigma_x^2 = \int_{-\infty}^{\infty} (x-\langle x\rangle)^2\,|\psi|^2\,dx \equiv \langle x^2\rangle - \langle x\rangle^2, \tag{160}$$

which is known as the *variance* of x. The square-root of this quantity, σ_x, is called the *standard deviation* of x. We generally expect the results of measurements of x to lie within a few standard deviations of the expectation value.

For instance, consider the normalized Gaussian wave packet [see Eq. (146)]

$$\psi(x) = \frac{e^{i\varphi}}{(2\pi\,\sigma^2)^{1/4}}\, e^{-(x-x_0)^2/(4\sigma^2)}.$$

The expectation value of x associated with this wavefunction is

$$\langle x\rangle = \frac{1}{\sqrt{2\pi\,\sigma^2}}\int_{-\infty}^{\infty} x\, e^{-(x-x_0)^2/(2\sigma^2)}\,dx.$$

Let $y = (x-x_0)/(\sqrt{2}\,\sigma)$. It follows that

$$\langle x\rangle = \frac{x_0}{\sqrt{\pi}}\int_{-\infty}^{\infty} e^{-y^2}\,dy + \frac{\sqrt{2}\,\sigma}{\sqrt{\pi}}\,\cancelto{0}{\int_{-\infty}^{\infty} y\, e^{-y^2}\,dy}.$$

However, the second integral on the right-hand side is zero, by symmetry. Hence, making use of Eq. (144), we obtain

$$\langle x\rangle = x_0.$$

The variance of x associated with the Gaussian wave packet (161) is

$$\sigma_x^2 = \frac{1}{\sqrt{2\pi\,\sigma^2}}\int_{-\infty}^{\infty}(x-x_0)^2\,\mathrm{e}^{-(x-x_0)^2/(2\,\sigma^2)}\,dx. \tag{165}$$

Let $y=(x-x_0)/(\sqrt{2}\,\sigma)$. It follows that

$$\sigma_x^2 = \frac{2\,\sigma^2}{\sqrt{\pi}}\int_{-\infty}^{\infty} y^2\,\mathrm{e}^{-y^2}\,dy. \tag{166}$$

However,

$$\int_{-\infty}^{\infty} y^2\,\mathrm{e}^{-y^2}\,dy = \frac{\sqrt{\pi}}{2}, \tag{167}$$

giving

$$\sigma_x^2 = \sigma^2. \tag{168}$$

This result is consistent with our earlier interpretation of σ as a measure of the spatial extent of the wave packet . It follows that we can rewrite the Gaussian wave packet (161) in the convenient form

$$\psi(x) = \frac{\mathrm{e}^{\,\mathrm{i}\,\varphi}}{(2\pi\,\sigma_x^2)^{1/4}}\,\mathrm{e}^{-(x-\langle x\rangle)^2/(4\,\sigma_x^2)}. \tag{169}$$

Ehrenfest's Theorem

A simple way to calculate the expectation value of momentum is to evaluate the time derivative of $\langle x\rangle$, and then multiply by the mass m: *i.e.*,

$$\langle p\rangle = m\,\frac{d\langle x\rangle}{dt} = m\,\frac{d}{dt}\int_{-\infty}^{\infty} x\,\vert\psi\vert^{\,2}\,dx = m\int_{-\infty}^{\infty} x\,\frac{\partial\vert\psi\vert^{\,2}}{\partial t}\,dx.$$

However, it is easily demonstrated that

$$\frac{\partial\vert\psi\vert^{\,2}}{\partial t} + \frac{\partial j}{\partial x} = 0$$

[this is just the differential form of Eq. (154)], where j is the probability current defined in Eq. (155). Thus,

$$\langle p\rangle = -m\int_{-\infty}^{\infty} x\,\frac{\partial j}{\partial x}\,dx = m\int_{-\infty}^{\infty} j\,dx,$$

where we have integrated by parts. It follows from Eq. (155) that

$$\langle p\rangle = -\frac{\mathrm{i}\,\hbar}{2}\int_{-\infty}^{\infty}\left(\psi^*\,\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\,\psi\right)dx = -\mathrm{i}\,\hbar\int_{-\infty}^{\infty}\psi^*\,\frac{\partial\psi}{\partial x}\,dx,$$

where we have again integrated by parts. Hence, the expectation value of the momentum can be written

$$\langle p\rangle = m\,\frac{d\langle x\rangle}{dt} = -\mathrm{i}\,\hbar\int_{-\infty}^{\infty}\psi^*\,\frac{\partial\psi}{\partial x}\,dx.$$

It follows from the above that

$$\begin{aligned}\frac{d\langle p\rangle}{dt} &= -\mathrm{i}\,\hbar\int_{-\infty}^{\infty}\left(\frac{\partial\psi^*}{\partial t}\,\frac{\partial\psi}{\partial x}+\psi^*\,\frac{\partial^2\psi}{\partial t\partial x}\right)dx\\ &= \int_{-\infty}^{\infty}\left[\left(\mathrm{i}\,\hbar\,\frac{\partial\psi}{\partial t}\right)^*\frac{\partial\psi}{\partial x}+\frac{\partial\psi^*}{\partial x}\left(\mathrm{i}\,\hbar\,\frac{\partial\psi}{\partial t}\right)\right]dx,\end{aligned}$$

where we have integrated by parts. Substituting from Schrödinger's equation (137), and simplifying, we obtain

$$\frac{d\langle p\rangle}{dt} = \int_{-\infty}^{\infty}\left[-\frac{\hbar^2}{2\,m}\frac{\partial}{\partial x}\left(\frac{\partial\psi^*}{\partial x}\frac{\partial\psi}{\partial x}\right)+V(x)\,\frac{\partial|\psi|^{\,2}}{\partial x}\right]dx = \int_{-\infty}^{\infty}V(x)\,\frac{\partial|\psi|^{\,2}}{\partial x}\,dx.$$

Integration by parts yields

$$\frac{d\langle p\rangle}{dt} = -\int_{-\infty}^{\infty}\frac{dV}{dx}\,|\psi|^{\,2}\,dx = -\left\langle\frac{dV}{dx}\right\rangle.$$

$$
\begin{aligned}
m \frac{d\langle x\rangle}{dt} &= \langle p\rangle, \\
\frac{d\langle p\rangle}{dt} &= -\left\langle \frac{dV}{dx} \right\rangle.
\end{aligned}
$$

Evidently, the expectation values of displacement and momentum obey time evolution equations which are analogous to those of classical mechanics. This result is known as *Ehrenfest's theorem*.

Suppose that the potential $V(x)$ is *slowly varying*. In this case, we can expand dV/dx as a Taylor series about $\langle x \rangle$. Keeping terms up to second order, we obtain

$$\frac{dV(x)}{dx} = \frac{dV(\langle x \rangle)}{d\langle x \rangle} + \frac{dV^2(\langle x \rangle)}{d\langle x \rangle^2}(x - \langle x \rangle) + \frac{1}{2}\frac{dV^3(\langle x \rangle)}{d\langle x \rangle^3}(x - \langle x \rangle)^2. \tag{180}$$

Substitution of the above expansion into Eq. (179) yields

$$\frac{d\langle p \rangle}{dt} = -\frac{dV(\langle x \rangle)}{d\langle x \rangle} - \frac{\sigma_x^2}{2}\frac{dV^3(\langle x \rangle)}{d\langle x \rangle^3}, \tag{181}$$

since $\langle 1 \rangle = 1$, and $\langle x - \langle x \rangle \rangle = 0$, and $\langle (x - \langle x \rangle)^2 \rangle = \sigma_x^2$. The final term on the right-hand side of the above equation can be neglected when the spatial extent of the particle wavefunction, σ_x, is much smaller than the variation length-scale of the potential. In this case, Eqs. (178) and (179) reduce to

$$m\frac{d\langle x \rangle}{dt} = \langle p \rangle, \tag{182}$$

$$\frac{d\langle p \rangle}{dt} = -\frac{dV(\langle x \rangle)}{d\langle x \rangle}. \tag{183}$$

These equations are *exactly equivalent* to the equations of classical mechanics, with $\langle x \rangle$ playing the role of the particle displacement. Of course, if the spatial extent of the wavefunction is negligible then a measurement of x is almost certain to yield a result which lies very close to $\langle x \rangle$. Hence, we conclude that quantum mechanics corresponds to classical mechanics in the limit that the spatial extent of the wavefunction (which is typically of order the de Boglie wavelength) is negligible. This is an important result, since we know that classical mechanics gives the correct answer in this limit.

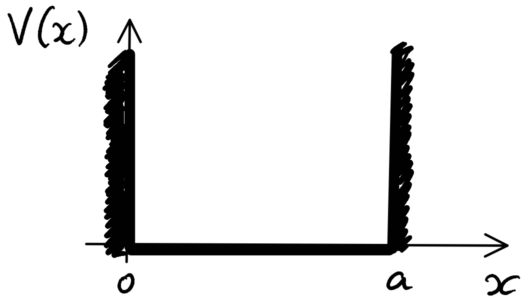
While applying Schrodinger equations in solving a problem, following boundary conditions must be fulfilled

Boundary Conditions

1. $\psi(x)$ must exist and satisfy the Schrödinger equation.
2. $\psi(x)$ and $d\psi/dx$ must be continuous.
3. $\psi(x)$ and $d\psi/dx$ must be finite.
4. $\psi(x)$ and $d\psi/dx$ must be single valued.
5. $\psi(x) \to 0$ fast enough as $x \to \pm\infty$ so that the normalization integral,

Application of Schrodinger equation

The infinite square well



$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le a \\ \infty, & \text{otherwise} \end{cases}$$

A particle in this potential is completely free, except at the two ends, where an infinite force prevents it from escaping.

Let's solve the Schrödinger equation!

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

First, we seek stationary states

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

We need to solve the time-independent Schrödinger equation

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

to find $\psi(x)$.

Outside of the well $\psi(x) = 0$.

Inside the well, where V= 0, the time-independent Schrödinger equation becomes:

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

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi$$

We introduce $k = \frac{\sqrt{2mE}}{\hbar}$ and write

$$\boxed{\frac{d^2\psi}{dx^2} = -k^2\psi} \qquad (E \geq 0)$$

Simple harmonic oscillator equation; its general solution is

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

where A and B are arbitrary constants that are generally obtained from boundary conditions.

What are the boundary conditions for $\psi(x)$?

Usually, both $\psi(x)$ and $\frac{d\psi}{dx}$ are continuous, but where $V \to \infty$ only the first applies.

Continuity of $\psi(x)$ requires that

$$\boxed{\psi(0) = \psi(a) = 0} \longleftarrow \text{Boundary conditions}$$

Now we can find out something about A and B

$$\psi(0) = A\sin 0 + B\cos 0 = B \Rightarrow \boxed{B = 0}$$

$$\psi(a) = A\sin ka \Rightarrow \text{either } A = 0$$

(trivial solution, discard)

or $\sin ka = 0 \Rightarrow$

$$ka = 0, \pm\pi, \pm 2\pi, \pm 3\pi \ldots$$

$k = 0$ also gives $\psi(x) = 0 \Rightarrow$ discard

Negative solutions give nothing new, since $\sin(-\theta) = -\sin(\theta)$ and sign can be absorbed into A.

Therefore, the distinct solutions are

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

and

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

and quantum particle in the infinite square well can not have just any energy. It has to be one of these special allowed values.

Now, we find A by normalizing $\psi(x)$:

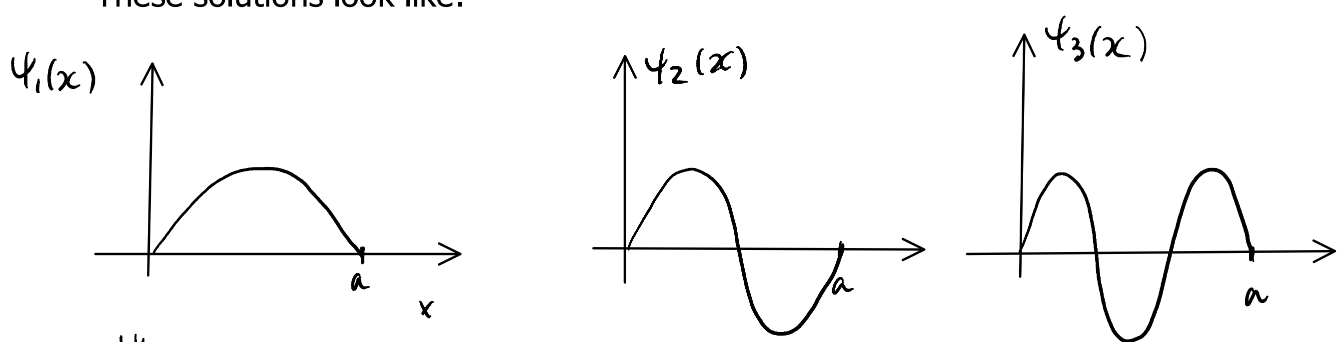
$$\int_a^b |A|^2 \sin^2 kx \, dx = |A|^2 \frac{a}{2} = 1 \quad \Rightarrow \quad |A|^2 = \frac{2}{a}$$

Global phase carries no significance in quantum mechanics, and we can pick positive root.

$$A = \sqrt{\frac{2}{a}}.$$

Therefore, $\boxed{\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)}$

These solutions look like:



ψ_1
carries
lowest energy
<u>It is called ground state.</u>

<u>Excited states</u>

The set of functions $\psi_n(x)$ has the following properties:

1. They are alternatively even and odd.

2. As you go up in energy, each successive state has one more node (zero-crossing).

3. They are mutually orthogonal, i.e.

$$\int \psi_m^*(x)\ \psi_n(x)\, dx = 0 \quad \text{if} \quad m \neq n$$

Also, if m = n $\quad \int \psi_m^*(x)\, \psi_m(x)\, dx = 1$ (normalization)

We can combine orthogonality and normalization into single statement

$$\boxed{\int \psi_m^*(x)\, \psi_n(x)\, dx = \delta_{mn}}$$

Kronecker delta

$$\boxed{\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n \\ 1, & \text{if } m = n \end{cases}}$$

We say that functions $\psi_n(x)$ are orthonormal.

4. They are complete, in the sense that any other function $f(x)$ can be expressed as a linear combination of them.

$$(1) \qquad f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a} x\right).$$

Note: the coefficients c_n may be evaluated using Fourier's trick:

multiply both sides of Eq. (1) by $\psi_m^*(x)$ and integrate

$$\int \psi_m^*(x) f(x)\, dx = \sum_{n=1}^{\infty} c_n \int \psi_m^*(x) \psi_n(x)\, dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m$$

$$c_n = \int_{-\infty}^{\infty} \psi_n^*(x)\, f(x)\, dx$$

Summary:

Stationary states for an infinite square well are:

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) e^{-i(n^2\pi^2\hbar^2/2ma^2)t}$$

The most general solution is

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) e^{-i(n^2\pi^2\hbar^2/2ma^2)t}$$

How to find c_n for a given initial function $\Psi(x,0)$?

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a} x\right) \Psi(x,0)\, dx$$

using $c_n = \int \psi_n^*(x) f(x)\, dx.$

$|c_n|^2$ tells you the probability that a measurement of the energy would yield the value E_n.

$$\sum_{n=1}^{\infty} |c_n|^2 = 1.$$