The Schrödinger Equation

We have seen that we can describe many properties of particles in terms of waves. We interpret the wave function, or the matter wave $\Psi$ proposed by de Broglie, as a probability distribution that allows us to calculate the probability of finding the particle at specific positions. The key question is how do the matter wave propagate.

The Schrödinger equation of a particle is the equation that allows us to calculate the wave function $\Psi$ of that particle if we provide information on the force acting on that particle (e.g. by specifying the potential energy associated with that force). The matter wave $\Psi$ proposed by de Broglie is expected to be a solution of the Schrödinger equation:

$$\Psi(x,t) = \sin\left(2\pi\left(\frac{x}{\lambda} - vt\right)\right) = \sin(kx - \omega t)$$

where $k = \frac{2\pi}{\lambda}$ is the wave number and $\omega = 2\pi\nu$ is the angular frequency. We expect that the Schrödinger equation is a differential equation. In classical physics we obtain the motion of a particle by solving the following differential equation:

$$F = \frac{dp}{dt} = m\frac{d^2x}{dt^2}$$

The Schrödinger equation must satisfy the following additional conditions:

1. The Schrödinger equation must be consistent with the de Broglie and the Einstein postulates:

   $$\lambda = \frac{h}{p}$$

   $$\nu = \frac{E}{h}$$

2. The energy associated with the wavefunction must be consistent with the following non-relativistic classical relation:

   $$E = \frac{p^2}{2m} + V$$

3. The Schrödinger equation must be linear in $\Psi$. This requires that if $\Psi_1$ and $\Psi_2$ are solutions than $a\Psi_1 + b\Psi_2$ is also a solution.
4. The potential $V$ may depend on $x$ and on $t$: $V(x, t)$. The special case of a free particle is obtained when $V = V_0$. **Note:** a constant potential implies $F = 0$.

Conditions 1 and 2 can be combined to produce the following requirement:

$$\frac{\hbar^2}{2m\lambda^2} + V(x, t) = \hbar \nu$$

We can rewrite this equation in terms of the angular frequency and the wave number and obtain

$$\frac{\hbar^2}{(2\pi)^2} \left( \frac{2\pi}{\lambda} \right)^2 + V(x, t) \equiv \frac{\hbar^2 k^2}{2m} + V(x, t) = \hbar \omega$$

Condition 3 requires that the Schrödinger equation only contains terms that are proportional to $\Psi$ and not terms that are proportional to for example $\Psi^2$. If consider the original matter wave $\Psi(x, t) = \sin(kx - \omega t)$ and the requirement we obtained from conditions 1 and 2, expressed in terms of $k$ and $\omega$, we conclude that the Schrödinger equation must contain terms proportional to the following partial differential terms:

- **$k^2$ term:** $\frac{\partial^2 \Psi}{\partial x^2} = \frac{\partial^2}{\partial x^2} \left[ \sin(kx - \omega t) \right] = -k^2 \sin(kx - \omega t)$
- **$\omega$ term:** $\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial t} \left[ \sin(kx - \omega t) \right] = -\omega \cos(kx - \omega t)$

It is easy to see that both of these differential terms are linear in $\Psi$. In order to make the Schrödinger equation linear in $\Psi$ the potential must appear in the following way: $V \Psi$.

A reasonable guess for the Schrödinger equation is an equation of the following form:

$$\alpha \frac{\partial^2 \Psi}{\partial x^2} + V \Psi = \beta \frac{\partial \Psi}{\partial t}$$

To describe a free particle, the wavefunction must be a solution of the following equation:

$$\alpha \frac{\partial^2 \Psi}{\partial x^2} + V_0 \Psi = \beta \frac{\partial \Psi}{\partial t}$$

We note that the original matter wave $\Psi$ is not a solution of this equation:
\[
\frac{\alpha \frac{\partial^2}{\partial x^2}[\sin(kx - \omega t)] + V[\sin(kx - \omega t)]}{\beta \frac{\partial}{\partial t}[\sin(kx - \omega t)]} = (-\alpha k^2 + V)[\sin(kx - \omega t)] \neq -\beta \omega \cos(kx - \omega t)
\]

We note that already in Chapter 4 we concluded that \( \Psi(x, t) = \sin(kx - \omega t) \) couldn’t describe a free particle. Consider the following wavefunction:

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

If this is a solution of our proposed differential equation we must require that

\[
\begin{align*}
\frac{\partial^2 \Psi}{\partial x^2} &= -k^2 \cos(kx - \omega t) - \gamma k^2 \sin(kx - \omega t) \\
\frac{\partial \Psi}{\partial t} &= \omega \sin(kx - \omega t) - \gamma \omega \cos(kx - \omega t)
\end{align*}
\]

\[
\begin{align*}
\alpha \frac{\partial^2 \Psi}{\partial x^2} + V_0 \Psi &= -\alpha k^2 \cos(kx - \omega t) - \alpha \gamma k^2 \sin(kx - \omega t) + V_0 \left( \cos(kx - \omega t) + \gamma \sin(kx - \omega t) \right) \\
\beta \frac{\partial \Psi}{\partial t} &= \beta \omega \sin(kx - \omega t) - \beta \gamma \omega \cos(kx - \omega t)
\end{align*}
\]

\[
\left( -\alpha k^2 + V_0 + \beta \gamma \omega \right) \cos(kx - \omega t) + \left( -\alpha \gamma k^2 + \gamma V_0 - \beta \omega \right) \sin(kx - \omega t) = 0
\]

In order for \( \Psi(x, t) = \cos(kx - \omega t) + \gamma \sin(kx - \omega t) \) to be a solution to our differential equation for all positions \( x \) and all times \( t \) we must require that

\[
\left( -\alpha k^2 + V_0 + \beta \gamma \omega \right) = 0 \quad \text{and} \quad \left( -\alpha \gamma k^2 + \gamma V_0 - \beta \omega \right) = 0
\]

If we multiply the first equation with \( \gamma \) and subtract the second equation we obtain

\[
\gamma \left( -\alpha k^2 + V_0 + \beta \gamma \omega \right) - \left( -\alpha \gamma k^2 + \gamma V_0 - \beta \omega \right) = \beta \gamma^2 \omega + \beta \omega = \beta \omega \left( \gamma^2 + 1 \right) = 0
\]

Assuming that \( \beta \) and \( \omega \) are not equal to 0, this equation requires that

\[
\gamma^2 + 1 = 0 \quad \Rightarrow \quad \gamma = \pm i
\]
With this value for \( \gamma \) we can rewrite the first condition required in order for \( \Psi(x,t) = \cos(kx - \omega t) + \gamma \sin(kx - \omega t) \) to be a solution of our differential equation in the following way:

\[
-\alpha k^2 + V_0 \pm i\beta \omega = 0 \quad \Rightarrow \quad -\alpha k^2 + V_0 = \pm i\beta \omega
\]

Comparing this equation to requirement 2 for our differential equation we conclude

\[
\begin{align*}
-\alpha k^2 + V_0 &= \pm i\beta \omega \\
\frac{\hbar^2 k^2}{2m} + V(x,t) &= \hbar \omega
\end{align*}
\]

\[
\Rightarrow \quad \alpha = -\frac{\hbar^2}{2m} \quad \text{and} \quad \beta = \pm i\hbar
\]

If we pick the + sign for \( \beta \) we obtain the **Schrödinger equation** for a free particle:

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V_0 \Psi = i\hbar \frac{\partial \Psi}{\partial t}
\]

The solution of this equation is

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

Note that the + sign in front of \( i \) is a consequence of our choice of a + sign for \( \beta \).

**Remarks on the Schrödinger equation and the wave function:**

1. The Schrödinger equation is a non-relativistic equation. We can only use it to describe particles moving at non-relativistic velocities.

2. The wavefunction \( \Psi(x,t) = \cos(kx - \omega t) + i\sin(kx - \omega t) \) is complex. It is a computational tool that allows us to calculate the probability of finding the particle at certain locations, but we cannot measure the wavefunction directly.

3. The physical relevant parameter we can obtain from the calculated wavefunction is the **probability density** \( P \) that is defined as \( P = \Psi^*\Psi \). \( \Psi^* \) is the complex conjugate of \( \Psi \). \( P(x,t) \, dx \) is the probability to find the particle at time \( t \) between \( x \) and \( x + dx \). In order for our definition of \( P \) to make sense, we must require that the wavefunction is normalized:

\[
\int_{-\infty}^{\infty} P(x,t) \, dx = \int_{-\infty}^{\infty} \Psi^*(x,t) \Psi(x,t) \, dx = 1
\]
This condition states that the particle must be somewhere between \( x = -\infty \) and \( x = +\infty \).
Using **Dirac notation** the normalization condition can be rewritten as

\[
\langle \Psi | \Psi \rangle = 1
\]

The expression \( \langle \psi | \varphi \rangle \) denotes taking the complex conjugate of the wavefunction on the left-hand-side and integrating the product \( \psi^* \varphi \). If \( a \) is a complex constant, we can show that the following rules apply

\[
\begin{align*}
\langle \psi | a \varphi \rangle &= a \langle \psi | \varphi \rangle \\
\langle a \psi | \varphi \rangle &= a^* \langle \psi | \varphi \rangle \\
\langle \psi | \varphi \rangle^* &= \langle \varphi | \psi \rangle \\
\langle \psi + \varphi | \psi \rangle &= \langle \psi | \psi \rangle + \langle \varphi | \varphi \rangle
\end{align*}
\]

**Example:**
Consider a particle that carries out simple harmonic motion. The potential associated with simple-harmonic motion only depends on \( x \) and is equal to

\[ V(x,t) = V(x) = \frac{1}{2}Cx^2 \]

where \( C \) is a positive constant. It is assumed that the equilibrium position is located at \( x = 0 \) m.
Let us first consider the motion from a classical point of view. The \( x \) position as function of time \( t \) can be described by a sine or cosine function; a sketch is shown in the Figure on the next page.
When we examine the motion of the particle, we often may want to know what the most probable and the least probable positions are. When we examine the position as function of time we note that the speed of the particle is lowest at the largest displacements; as a consequence, the particle will spend the largest fraction of its time at these positions. The speed of the particle is the largest when it crosses the equilibrium position; as a consequence, the particle will spend the smallest fraction of its time around its equilibrium position. We thus conclude:

1. The most probable values of \( x \) are \(+A\) and \(-A\).
2. The least probable value of \( x \) is 0.
Now consider the motion from a quantum mechanical point of view. The Schrödinger equation for the particle is

\[ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2}Cx^2 \psi = i\hbar \frac{\partial \psi}{\partial t} \]

The solution of this wavefunction is

\[ \Psi(x,t) = Ae^{-\left(\frac{\sqrt{Cm/2\hbar}}{\pi}\right)^2}e^{-\left(i/2\right)\sqrt{Cm/\hbar} t} \]

We can verify that this wavefunction is a solution by substituting it in the Schrödinger equation. To determine the constant \( A \) we need to use the requirement that \( \langle \psi | \psi \rangle = 1 \):

\[
\langle \Psi | \Psi \rangle = \int_{-\infty}^{\infty} \Psi^* \psi \, dx = \int_{-\infty}^{\infty} \left[A^* e^{-\left(\sqrt{Cm/2\hbar}\right)^2 x^2} e^{-\left(i/2\right)\sqrt{Cm/\hbar} t} \right]^* \left(A e^{-\left(\sqrt{Cm/2\hbar}\right)^2 x^2} e^{-\left(i/2\right)\sqrt{Cm/\hbar} t} \right) \, dx = A^* A \int_{-\infty}^{\infty} e^{-\left(\sqrt{Cm/\hbar}\right)^2 x^2} \, dx = A^* A \frac{\sqrt{\pi}}{\sqrt{Cm / \hbar}} = 1
\]

If we assume that \( A \) is a real number we obtain the following expression for \( A \)

\[ A = \sqrt{\frac{\sqrt{\sqrt{Cm / \hbar}}}{\sqrt{\pi}}} = \sqrt{\frac{\sqrt{Cm}}{\sqrt{\pi\hbar}}} = \frac{(Cm)^{1/8}}{(\pi\hbar)^{1/4}} \]

The probability distribution of the wave function is given by
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\[ P(x,t) = \Psi^* \Psi = A^* A e^{-\left(\sqrt{\frac{Cm}{\hbar}}\right)^2 x^2} = \]
\[ = \frac{(Cm)^{1/4}}{(\pi \hbar)^{1/2}} e^{-\left(\sqrt{\frac{Cm}{\hbar}}\right)^2 x^2} \]

Comparing the probability distributions obtained from the classical model and the quantum mechanical model (see Figure on the right) we see that the location of the most probable and the least probable positions differ significantly for these two models.

**Predicting the future**

If we know the wavefunction \( \Psi(x,t) \) at time \( t = 0 \) we can use the Schrödinger equation to determine \( \Psi(x,t) \) at all times. But, does this imply that we can predict the future with great accuracy? The answer to this question is no. We need to remember that we can only measure \( \Psi^* \Psi \). It is impossible to completely determine \( \Psi \) from the measured \( \Psi^* \Psi \). And we are thus not able to fully specify \( \Psi(x,0) \).

**Expectation values**

In order to examine the motion of a particle we may want to know what the expectation value of its position is. The expectation value of \( x \) is defined as

\[ \langle x \rangle = \int_{-\infty}^{+\infty} x P(x,t) \, dx = \int_{-\infty}^{+\infty} \Psi^* x \Psi \, dx \]

This is frequently written as

\[ \langle x \rangle = \langle \Psi | x \Psi \rangle \]

If the wavefunction is even, \( \Psi(x,t) = \Psi(-x,t) \), the expectation value of \( x \) will be zero. This is a result of the fact that \( x \) is odd function with respect to \( x = 0 \). If the wavefunction is odd, \( \Psi(x,t) = -\Psi(-x,t) \), the expectation value of \( x \) will not be equal to zero.
The expectation value of an operator $O$ is defined as

$$\langle O \rangle = \langle \Psi | O \Psi \rangle$$

Since the expectation value of an operator represents a measurable quantity, it must be real. Even though the wavefunction are in general complex functions, the integral used to determine the expectation value must be real.

If the operator depends only on the position $x$, the evaluation of its expectation value is straightforward. However, when the operator depends on the momentum $p$, the calculation of the expectation value is more complicated. Consider first the expectation value of $p$.

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* p \Psi \; dx$$

In order to evaluate this integral we need to express $p$ in terms of $x$. This is possible in classical physics, but the uncertainty principle in quantum mechanics prevents us from expressing $p$ as a function of $x$. In order to express $p$ in terms of $x$ and $t$ we note that when we differentiate the wavefunction of a free particle with respect to $x$ we obtain

$$\frac{\partial \Psi}{\partial x} = i k \Psi$$

Since $k$ is related to the momentum $p$ we can rewrite this expression as

$$\frac{\partial \Psi}{\partial x} = i \frac{p}{\hbar} \Psi \implies p \Psi = -i \hbar \frac{\partial \Psi}{\partial x}$$

In order to calculate the expectation of $p$ we replace $p$ with the differential operator $-i \hbar (\partial / \partial x)$. The expectation value of $p$ is thus equal to

$$\langle p \rangle = -i \hbar \int_{-\infty}^{\infty} \left[ \Psi^* \frac{\partial \Psi}{\partial x} \right] dx = -i \hbar \left\langle \Psi \left| \frac{\partial}{\partial x} \Psi \right\rangle \right.$$
Since $\omega$ is related to the energy $E$ we can rewrite this expression as

$$\frac{\partial \Psi}{\partial t} = -i \frac{E}{\hbar} \Psi \Rightarrow E\Psi = +i\hbar \frac{\partial}{\partial t} \Psi$$

In order to calculate the expectation of $E$ we replace $E$ with the differential operator $i\hbar (\partial / \partial t)$. The expectation value of $E$ is thus equal to

$$\langle E \rangle = i\hbar \int_{-\infty}^{\infty} \left[ \Psi^* \frac{\partial}{\partial t} \Psi \right] dx = i\hbar \left\langle \Psi \left| \frac{\partial}{\partial t} \Psi \right. \right\rangle$$

In general, the expectation value of a function $f(x, p, t)$ is equal to

$$\langle f(x, p, t) \rangle = \int_{-\infty}^{\infty} \left[ \Psi^* f(x, -i\hbar \frac{\partial}{\partial x}, t) \right] \Psi \right\rangle = \left\langle f \left| \Psi \right| \frac{-i\hbar \frac{\partial}{\partial x}, t \right\rangle \right\rangle$$

**Example**

Consider the example of a particle that is free to move inside a box with walls located at $x = \pm a/2$ but it not able to move in the region outside the box. The wavefunction describing this particle is equal to

$$\Psi(x, t) = \begin{cases} 
0 & x \leq -\frac{1}{2}a \\
A \cos \left( \frac{\pi x}{a} \right) e^{-iEt/\hbar} & -\frac{1}{2}a < x < \frac{1}{2}a \\
0 & x \geq \frac{1}{2}a 
\end{cases}$$

The constant $A$ must be defined such that the integral of the probability distribution is equal to 1. Assuming that $A$ is a real number, this requires that

$$1 = \int_{-\infty}^{\infty} \Psi^* \Psi \ dx = A^2 \int_{-a/2}^{a/2} \cos^2 \left( \frac{\pi x}{a} \right) \ dx = A^2 \frac{a}{2} \Rightarrow A = \sqrt{\frac{2}{a}}$$

The expectation value of $x$ is equal to
\[ \langle x \rangle = \int_{-\infty}^{\infty} \Psi^* x \Psi \, dx = \frac{2}{a} \int_{-a/2}^{a/2} \cos^2 \left( \frac{\pi x}{a} \right) x \, dx = 0 \]

The expectation value of \( x^2 \) is equal to

\[ \langle x^2 \rangle = \int_{-\infty}^{\infty} \Psi^* x^2 \Psi \, dx = \frac{2}{a} \int_{-a/2}^{a/2} \cos^2 \left( \frac{\pi x}{a} \right) x^2 \, dx = \frac{2}{a} \left( \frac{a^3}{4\pi^2} \left( \frac{\pi^2}{6} - 1 \right) \right) = \frac{a^2}{2\pi^2} \left( \frac{\pi^2}{6} - 1 \right) \]

The mean-square deviation of \( x \) is a measure of the spread of \( x \) values about the expectation value of \( x \) and is defined using the following relation:

\[ \langle \Delta x \rangle^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 - 2x \langle x \rangle + \langle x \rangle^2 \rangle = \langle x^2 \rangle - 2 \langle x \rangle \langle x \rangle + \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2 \]

The spread in \( x \) is thus equal to

\[ \Delta x = \sqrt{\langle \Delta x \rangle^2} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{a^2}{2\pi^2} \left( \frac{\pi^2}{6} - 1 \right) - 0} = \sqrt{\frac{a^2}{2\pi^2} \left( \frac{\pi^2}{6} - 1 \right)} \approx 0.182a \]

The expectation value of \( p \) is equal to

\[ \langle p \rangle = -i \hbar \int_{-a/2}^{a/2} \left[ \Psi^* \frac{\partial}{\partial x} \Psi \right] \, dx = -i \hbar \left( \frac{2}{a} \right) \int_{-a/2}^{a/2} \left( -\frac{\pi}{a} \right) \cos \left( \frac{\pi x}{a} \right) \sin \left( \frac{\pi x}{a} \right) \, dx = 0 \]

The expectation value of \( p^2 \) is equal to

\[ \langle p^2 \rangle = -\hbar^2 \int_{-\infty}^{\infty} \left[ \frac{\partial^2}{\partial x^2} \right] \Psi dx = -\hbar^2 \left( \frac{2}{a} \right) \int_{-a/2}^{a/2} \cos^2 \left( \frac{\pi x}{a} \right) x^2 \, dx = \frac{2}{a} \left( \frac{\hbar^2}{a^2} \right) \frac{\pi^2}{2} = \left( \frac{\hbar}{a} \right)^2 \]

The spread in \( p \) is thus equal to

\[ \Delta p = \sqrt{\langle \Delta p \rangle^2} = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\left( \frac{\hbar}{a} \right)^2} - 0 = \left( \frac{\hbar}{a} \right) \]

The product of the spread in \( x \) and the spread in \( p \) is thus equal to

\[ \Delta x \Delta p = (0.182a) \left( \frac{\hbar}{a} \right) = 0.570\hbar \approx \frac{1}{2} \hbar \]
which is consistent with the uncertainty principle.

**Solving the Schrödinger equation**

If we know the potential of the system we are studying, we can use the Schrödinger equation to obtain the wavefunction that describes the behavior of the system.

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

In order to look at solutions of this equation we will make the following assumptions:

- The potential \(V(x,t)\) does not depend on time \(t\): \(V(x,t) = V(x)\)
- The wavefunction can be rewritten as \(\Psi(x,t) = \psi(x)\phi(t)\).

With these assumptions the Schrödinger equation can be rewritten as

\[-\frac{\hbar^2}{2m} \frac{\partial^2 (\psi(x)\phi(t))}{\partial x^2} + V(x)(\psi(x)\phi(t)) = i\hbar \frac{\partial (\psi(x)\phi(t))}{\partial t}\]

differentiate

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} \phi(t) + V(x)\psi(x)\phi(t) = i\hbar \frac{\partial \phi(t)}{\partial t} \psi(x)\]

divide by \(\psi(x)\phi(t)\)

\[-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) = i\hbar \frac{1}{\phi(t)} \frac{\partial \phi(t)}{\partial t}\]

The left-hand side of the last equation only depends on \(x\) and the right-hand side of the last equation only depends on \(t\). This equation can thus only be satisfied for all \(x\) and for all \(t\) if the left- and right-hand sides are equal to a constant.

\[-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) = G \quad \text{and} \quad i\hbar \frac{1}{\phi(t)} \frac{\partial \phi(t)}{\partial t} = G\]

Let’s first consider the time-dependent differential equation:

\[i\hbar \frac{1}{\phi(t)} \frac{\partial \phi(t)}{\partial t} = G \quad \Rightarrow \quad \frac{\partial \phi(t)}{\partial t} = -\frac{i}{\hbar} G\phi(t)\]

The general solution of this equation is
$\varphi(t) = A e^{-iGt/h} = e^{-iGt/h}$

The time dependence of this solution can be described in terms of the angular frequency $\omega = G/h$. The corresponding frequency is equal to

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \left( \frac{G}{h} \right) = \frac{G}{h}$$

We can compare this frequency with the frequency that is consistent with Einstein’s postulate:

$$\nu = \frac{E}{h}$$

to conclude that $G = E$ where $E$ is the energy of the system. The time-dependent component of the wavefunction is thus given by

$$\varphi(t) = e^{-iEt/h}$$

The differential equation for the position-dependent wavefunction now becomes equal to

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

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

This equation can be rewritten as

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

This equation is called the time-independent Schrödinger equation. The solutions to this equation are called eigenfunctions.

The eigenfunctions have the following properties:

- $\psi(x)$ and $d\psi(x)/dx$ must be finite for all $x$.
- $\psi(x)$ and $d\psi(x)/dx$ must be single valued for all $x$.
- $\psi(x)$ and $d\psi(x)/dx$ must be continuous for all $x$. 
These requirements are a consequence of the requirements that the expectation values of the wavefunctions behave in reasonable ways. The functions shown in the Figure on page 12 do not satisfy some of these conditions, and can thus not represent an eigenfunctions.

Consider the potential shown in the Figure on the right. In the region between $x'$ and $x''$, the difference $V - E$ is negative. In the region below $x'$ or above $x''$ the difference $V - E$ is positive. We can lean quite a bit about the shape of the wavefunction by applying the conditions that need to be satisfied by the eigenfunctions. Consider for the region for which $x > x''$. In this region $V(x) - E > 0$. If $\psi(x) > 0$ the Schrödinger equation requires that $\frac{\partial^2 \psi(x)}{\partial x^2} > 0$. If $\psi(x) < 0$ the Schrödinger equation requires that $\frac{\partial^2 \psi(x)}{\partial x^2} < 0$. The same conditions apply in the region for which $x < x'$.

Now consider the region for which $x' < x < x''$. In this region $V(x) - E < 0$. If $\psi(x) > 0$ the Schrödinger equation requires that $\frac{\partial^2 \psi(x)}{\partial x^2} < 0$. If $\psi(x) < 0$ the Schrödinger equation requires that $\frac{\partial^2 \psi(x)}{\partial x^2} > 0$.

The consequences of these conditions on the shape of the wavefunctions are schematically shown in the Figure on the right.

Consider the consequence of these observations on possible wavefunctions that are solutions of the time-independent Schrödinger equation. The Figure on the right shows three possible wavefunctions that have the same value at $x = x_0$. Function # 1 has a minimum value in the region where $x > x'$ and its slope will keep increasing for at positions larger than this position. It is not a possible eigenfunctions since it will approach infinity when $x$ approaches infinity. Function # 2 will be zero in the region where $x > x'$. At larger positions, the slope will become increasingly more negative and the eigenfunctions will approach minus infinity when $x$ approaches infinity. Only function #
3 can be a possible eigenfunction. This is an acceptable eigenfunction if it does not have a minimum at any finite value of $x$.

The shape of the eigenfunction can also provide us with information on the energy of the system that is being described by it. Consider the three eigenfunctions that are shown in the Figure on the right. Consider the position $x_0$. At this position, the values of the eigenfunctions are all the same. These eigenfunctions are solutions of the time-independent Schrödinger equation:

$$\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{2m}{\hbar^2} (V(x,t) - E) \psi(x) \quad \Rightarrow \quad \begin{cases} \frac{\partial^2 \psi_1}{\partial x^2}\bigg|_{x_0} = \frac{2m}{\hbar^2} (V(x_0,t) - E_1) \psi_1(x_0) \\ \frac{\partial^2 \psi_2}{\partial x^2}\bigg|_{x_0} = \frac{2m}{\hbar^2} (V(x_0,t) - E_2) \psi_2(x_0) \\ \frac{\partial^2 \psi_3}{\partial x^2}\bigg|_{x_0} = \frac{2m}{\hbar^2} (V(x_0,t) - E_3) \psi_3(x_0) \end{cases}$$

This equation has to be satisfied at all positions, and thus also at position $x_0$. When the number of nodes of a wavefunction increases, its maximum slope will also increase, and so will the rate with which the slope is changing. For the three wavefunctions shown in the Figure we thus conclude that

$$\left| \frac{\partial^2 \psi_3}{\partial x^2}\bigg|_{x_0} \right| > \left| \frac{\partial^2 \psi_2}{\partial x^2}\bigg|_{x_0} \right| > \left| \frac{\partial^2 \psi_1}{\partial x^2}\bigg|_{x_0} \right|$$

This requires that

$$\left| \frac{2m}{\hbar^2} (V(x_0,t) - E_3) \psi_3(x_0) \right| > \left| \frac{2m}{\hbar^2} (V(x_0,t) - E_2) \psi_2(x_0) \right| > \left| \frac{2m}{\hbar^2} (V(x_0,t) - E_1) \psi_1(x_0) \right|$$
Since the values of the wavefunctions are the same at position $x_0$ and since $E > V$ at this position (which we can conclude based on the shape of the wavefunctions), we can rewrite the last equation in the following way:

$$E_3 - V(x_0, t) > E_2 - V(x_0, t) > E_1 - V(x_0, t) \Rightarrow E_3 > E_2 > E_1$$

The shape of the wavefunctions thus tells us quite a bit about the associated energies.