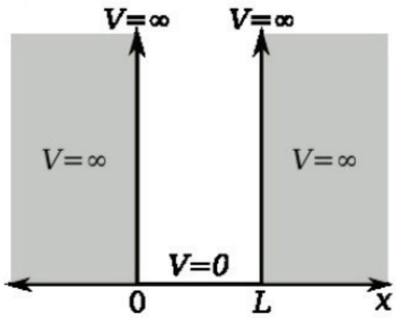
Particle in a box

A simple system for which the time-indenpent Schrödinger equation can be solved exactly is the particle in a box. The particle in a box is represented by a small region in space where inside the box the potential is zero and at its wall and out side is infinite. Thus, the particle is free to move inside to box since it experience no forces, but remain in the box since the walls are infinitely high. While this is system might seem very abstract it can to some degree be used to gain insight into the optical properties of e.g. quantum dots and conjugated molecules.

Particle in a 1D-box



The particle in a 1D box of length L is represented by a potential given by

$$V(x) = \begin{cases} \infty & \text{for x} \leqslant 0 \\ 0 & \text{for } 0 < \text{x} < \text{L} \\ \infty & \text{for x} \geqslant \text{L} \end{cases}$$

From this we can see that outside the box the wavefunction must be zero since

$$\infty \psi_I(x) = \frac{\hbar^2}{2m}\frac{d^2\psi_I(x)}{dx^2}$$
$$\psi_I(x) = \frac{1}{\infty}\frac{\hbar^2}{2m}\frac{d^2\psi_I(x)}{dx^2} = 0$$

Therefore, we only need to solve the Schrödinger equation for the particle inside the box

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

$$\begin{aligned}
\frac{\hbar^2}{2m}\frac{d^2\psi_{II}(x)}{dx^2}+E\psi_{II}(x) &= 0\\
\frac{d^2\psi_{II}(x)}{dx^2}+\frac{2m}{\hbar^2}E\psi_{II}(x) &= 0\\
y''+qy &= 0
\end{aligned}$$

Which we recognize as a linear homogenous second-order differential equation with constant coefficients. We know that the solution is of the form $y=e^{sx}$ and we can write the auxiliary equation as

$$\begin{aligned}
s^2+2mE\hbar^{-2} &= 0\\
s^2+q &= 0\\
s &= \pm\sqrt{-q}\\
s &= \pm i\sqrt{q}\\
s &= \pm i\sqrt{2mE}/\hbar
\end{aligned}$$

Therefore, the solution is given by

$$\psi_{II}(x)=c_1\exp^{i\sqrt{2mE}x/\hbar}+c_2\exp^{-i\sqrt{2mE}x/\hbar}$$

We can now manipulate the solution in the following way

$$\psi_{II}(x)=c_1\exp(i\theta)+c_2\exp(-i\theta)$$

where $\theta=\sqrt{2mE}x/\hbar$. Using that $\exp(i\theta)=\cos(\theta)+\sin(\theta)$ we get

$$\begin{aligned}
\psi_{II}(x) &= c_1\exp(i\theta)+c_2\exp(-i\theta)\\
&= c_1\cos(\theta)+ic_1\sin(\theta)+c_2\cos(-\theta)+ic_2\sin(-\theta)\\
&= c_1\cos(\theta)+ic_1\sin(\theta)+c_2\cos(\theta)-ic_2\sin(\theta)\\
&= (c_1+c_2)\cos(\theta)+(ic_1-ic_2)\sin(\theta)\\
&= A\cos(\theta)+B\sin(\theta)
\end{aligned}$$

where A and B are two new arbitrary constants. We can determine these constants by applying the boundary conditions. We will postulate, reasonable, that the wavefunction needs to be continuous, therefore, we require that the wavefunction is also continuous at the boundary

$$\begin{aligned}
\lim_{x\to 0}\psi_I &= \lim_{x\to 0}\psi_{II}\\
0 &= \lim_{x\to 0}\psi_{II}\left\{A\cos(\theta)+B\sin(\theta)\right\}\\
0 &= A\cos(0)+B\sin(0)=A
\end{aligned}$$

where n is the quantum number. Draw the first few solution of the wave-function on the board, and the square of the solutions as well. Compare this with what is expected from classical physics ? Where is the particle ? What happens when n goes toward ∞? In this limit we reach the classical results of uniform probability density. This is known as the Bohr correspondence principle.

We know that the wavefunction is normalized so

$$\int_{-\infty}^{\infty} \psi_i^* \psi_i dx = 1$$

However, what is we use two wavefunctions with different quantum numbers

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = 2/L \int_0^L \sin(n_i \pi x/L) \sin(n_j \pi x/L) dx = 0$$

where we have used the integral table in Appendix. There, two wavefunctions with different quantum numbers are orthogonal

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = \delta_{ij}$$

where δ_{ij} is Kronecker delta, which is one if $i = j$ otherwise zero.

Therefore,

$$\psi_{II}(x) = B\sin(\theta)$$

Applying the boundary condition at $x = L$ we get

$$\psi_{II}(x) = B\sin(\sqrt{2mE}L/\hbar) = 0$$

This is satisfied for

$$\sqrt{2mE}L/\hbar = \pm n\pi \; n = 1, 2, 3, \cdots$$

What about $n = 0$? This corresponds to $\psi_{II}(x) = 0$ and thus no particle. This gives us the energy

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

Therefore, we see that quantization of the energy for the particle in a box comes directly as a results of the Schrödinger equation. The wavefunction is

$$\psi_{II}(x) = B\sin\left(\frac{n\pi x}{L}\right), \;\; n = 1, 2, 3, \cdots$$

How do we then determine B? We use the normalization requirement

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

$$\int_{0}^{L} |\psi(x)|^2 dx = 1$$

$$|B|^2 \int_{0}^{L} \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

$$|B|^2 \frac{L}{2} = 1$$

$$|B| = \sqrt{2/L}$$

where we have used that

$$\int \sin^2 bx dx = \frac{x}{2} - \frac{1}{4b}\sin(2bx)$$

from Table A.5 on page 721 on Levine. Therefore, the final solution for the wavefunction is

$$\psi_{II}(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \;\; n = 1, 2, 3, \cdots$$