

# Analytic solution of the Schrödinger equation: Particle in a box

## Notes on Quantum Mechanics

<http://quantum.bu.edu/notes/QuantumMechanics/ParticleInABox.pdf>  
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One way to work with the curvature form of the Schrödinger equation,

$$\text{curvature of } \psi \text{ at } x \propto - \text{kinetic energy at } x \times \psi \text{ at } x,$$

is try to guess what wavefunctions,  $\psi$ , satisfy it. For systems in which the kinetic energy changes with position in complicated ways, systematic implementation of this so-called analytic approach typically requires sophisticated mathematical machinery and so it not as easy to understand as the visual approach we will use.

However, there is one example of the analytic approach that is very easy to understand, namely the case where a particle of mass  $m$  is confined in a one-dimensional region of width  $L$ ; in this region it moves freely but it is not able to move outside this region. Such a system is called a *particle in a box*. It is one of the most important example quantum systems in chemistry, because it helps us develop intuition about the behavior on electrons confined in molecules.

To use the analytical method, we begin by writing the Schrödinger equation more precisely as

$$\text{curvature of } \psi \text{ at } x = - \frac{2m}{\hbar^2} \times \text{kinetic energy at } x \times \psi \text{ at } x.$$

The reason the particle is able to move freely in the specified region,  $0 \leq x \leq L$  (inside the "box"), is that its potential energy there is zero. The way the particle is confined to the specified region is by considering the potential energy outside this region to be infinite. The consequence is that the wavefunction is not able to penetrate at all into regions  $x < 0$  and  $L < x$ , for if it did its curvature there would be infinite, and so it would diverge to infinity and thus not be a physically acceptable wavefunction. The result is that we need to consider the wavefunction only in the allowed region and there the kinetic energy is just the total energy,

$$\text{kinetic energy at } 0 \leq x \leq L = E - \text{potential energy at } 0 \leq x \leq L = E - 0 = E$$

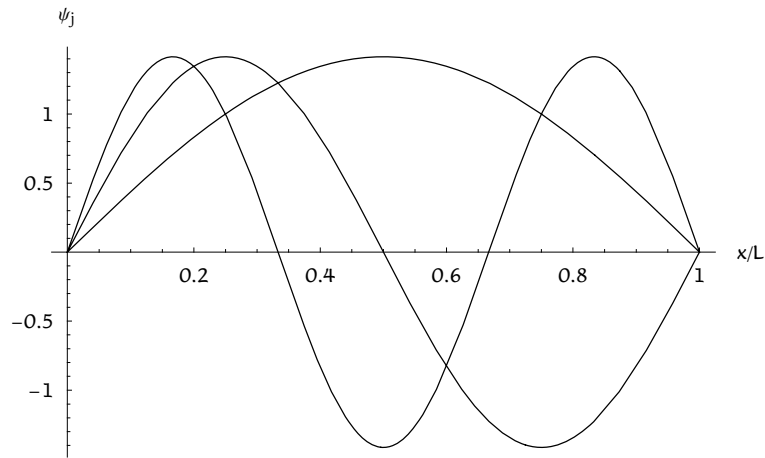
This means that the Schrödinger equation inside the box is

$$\text{curvature of } \psi \text{ at } x = - \frac{2mE}{\hbar^2} \times \psi \text{ at } x, \quad 0 \leq x \leq L$$

To "solve" this equation, we need a wavefunction,  $\psi$ , whose second derivative is proportional to the function itself. The trigonometric functions  $\sin(ax)$  and  $\cos(ax)$  have this behavior. Since we know that the wavefunction and its slope have to vary smoothly, so that its curvature has a value at each point, but also since we know that the wavefunction must be 0 at the edges of the box,  $x = 0$  and  $x = L$ , the functions we need are sine functions that have zeros at  $x = 0$  and  $x = L$ . That is, the acceptable solutions to the Schrödinger equation are sine functions with an integer number,  $j$ , of half-wavelengths (loops) in the region  $0 \leq x \leq L$ ,

$$\psi_j = \sqrt{2/L} \sin(j\pi x/L)$$

Here are the functions for  $j = 1, 2,$  and  $3$ :



Normalized wavefunctions for a particle in a box of width  $L$ , with one, two and three loops.

The factor  $\sqrt{2/L}$  insures that the probability of finding the particle somewhere in the box is 1,

$$\int_0^L |\psi_j(x)|^2 dx = \int_0^L \frac{2}{L} \sin^2\left(j\pi \frac{x}{L}\right) dx = 1,$$

that is, that the wavefunction is normalized.

Once we have the wavefunctions, we can use them in the Schrödinger equation to determine the corresponding energies. To do this we need to use the expression for the curvature of a sine function (discussed in the notes on calculus),

$$\begin{aligned} \text{curvature of } \psi_j \text{ at } x &= \sqrt{2/L} \frac{d^2}{dx^2} \sin(j\pi x/L) \\ &= \sqrt{2/L} \frac{j\pi}{L} \frac{d}{dx} \cos(j\pi x/L) \\ &= -\sqrt{2/L} \left(\frac{j\pi}{L}\right)^2 \sin(j\pi x/L) \\ &= -\left(\frac{j\pi}{L}\right)^2 \times \psi_j \text{ at } x \end{aligned}$$

Substituting this expression in the Schrödinger equation gives,

$$\text{curvature of } \psi \text{ at } x = -\left(\frac{j\pi}{L}\right)^2 \times \psi_j \text{ at } x = -\frac{2mE_j}{\hbar^2} \times \psi \text{ at } x, \quad 0 \leq x \leq L,$$

and so that

$$\left(\frac{j\pi}{L}\right)^2 = \frac{2mE_j}{\hbar^2}.$$

This result means that the energy of the particle described by the  $j$ -th wavefunction in the box is

$$E_j = \frac{j^2 \pi^2 \hbar^2}{2 m L^2} = \frac{j^2 \pi^2 (h/2\pi)^2}{2 m L^2} = \frac{j^2 h^2}{8 m L^2}.$$

The key aspects of this result are that the energy increases quadratically with the number of loops in the wavefunction; it decreases quadratically with the width of the confinement; and it decreases in proportion to the mass of the particle.

Derive the same energy expression by using de Broglie's relation,  $p = h/\lambda$ , together with the fact that inside the box the energy of the particle is entirely kinetic, that is, inside the box,  $E = p^2/2m$ .

## ■ Modelling dye-molecule absorption

To get some experience with these results, let's use them to estimate the properties on an electron confined in a molecule. Here is an expression for the wavelength, in nm, of light corresponding to the lowest energy transition,  $j = 1 \rightarrow j = 2$ , of an electron confined in a one-dimensional region of length  $L$ ,

$$\lambda_{1 \rightarrow 2} = \frac{hc}{\Delta E_{1 \rightarrow 2}} = \frac{8cmL^2}{3h}.$$

Show that this expression is correct.

The reason carrots are orange is that the carotene molecules that they contain absorb light in the blue region of the visible spectrum. Since carotene,  $C_{40}H_{56}$ , is a long hydrocarbon chain, one way to think about its absorption of blue light is to consider it as being due to an electron confined as a particle in a box about the length of the molecule.

Calculate the width of the box, in  $\text{\AA} = 1 \times 10^{-10} m$ , that would correspond to an electron absorbing blue light, 450 nm, in the transition from  $\psi_1$  to  $\psi_2$ . Answer: 6.7  $\text{\AA}$ .

## ■ Zero-point energy

One very important result of this analysis is that the lowest energy a particle can have in a one dimensional box is *not* zero, but instead

$$E_1 = \frac{h^2}{8mL^2}.$$

This lowest energy is called the *zero-point energy*. The reason the zero point energy is always present is that the wavefunction must always have some curvature in some places, and so there must always be some kinetic energy. All quantum systems have zero point energy.

Calculate the zero point energy due to the electron assumed to account for carotene absorption of blue light for a mole of carotene molecules. Answer: 80 kJ.

## ■ Two- and three-dimensional confinement

It is easy to extend the model of a particle confined to two- and three-dimensional regions. The Schrödinger equation in two dimension is

$$\begin{aligned} & \text{curvature along } x \text{ of } \psi \text{ at } (x, y) + \text{curvature along } y \text{ of } \psi \text{ at } (x, y) \\ &= -\frac{2m}{\hbar^2} \times \text{kinetic energy at position } (x, y) \times \psi \text{ at } (x, y), \end{aligned}$$

and it has a similar expression for three dimensions. As long as the kinetic energy along each dimension is not affected by the position in the other dimensions, then the Schrödinger equation is said to be *separable*. What this means is that then the *ratio* of the curvature and the wavefunction in each dimension is constant for all positions.

Here is a way to see that this is so, for the example of confinement in a two dimensional region,  $0 \leq x \leq L_x$ ,  $0 \leq y \leq L_y$ , by infinite potential energy at the edges of the regions but with zero potential energy inside the regions. Since everywhere inside the region the particle has zero potential energy, this means that its kinetic energy is just the total energy and so is constant. We can thus write the Schrödinger equation in two dimension for this case a little more simply as

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

To separate motion in  $x$  and  $y$  we try expressing the wavefunction as a product of wavefunctions for each dimension,

$$\psi(x, y) = X(x) Y(y).$$

With this assumed factoring of the overall wavefunction we can write the Schrödinger equation as

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} = -\frac{2m}{\hbar^2} E.$$

Use the assumed factorization to obtain this equation.

Now, the right hand side of this equation, for a given total (kinetic) energy is a number with units  $\text{length}^{-2}$ .

Show that this dimensional analysis is correct.

For the sake of discussion, let's assume the right hand side evaluates to  $-0.517 \text{ \AA}^{-2}$ , and that at  $x = 0.3 L_x$  and  $y = 0.7 L_y$  the terms on the left hand side evaluate to

$$\left( \frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} \right)_{x=0.3 L_x} = 0.411 \text{ \AA}^{-2} \text{ and } \left( \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} \right)_{y=0.7 L_y} = 0.106 \text{ \AA}^{-2},$$

so that in terms of numerical values the Schrödinger equation at  $(x, y) = (0.3 L_x, 0.7 L_y)$  is

$$-0.411 \text{ \AA}^{-2} - 0.106 \text{ \AA}^{-2} = -0.517 \text{ \AA}^{-2}.$$

Next, consider the value of  $1/X(x) \partial^2 X(x)/\partial x^2$  at another value of  $x$ , say  $x = 0.4 L_x$ ? Let's say the new value is  $-q \text{ \AA}^2$ ,

$$\left( \frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} \right)_{x=0.4 L_x} = -q \text{ \AA}^{-2}.$$

Since we have not changed the value of  $y$ , in terms of numerical values the Schrödinger equation at  $(x, y) = (0.4 L_x, 0.7 L_y)$  is

$$-q \text{ \AA}^{-2} - 0.106 \text{ \AA}^{-2} = -0.517 \text{ \AA}^{-2}.$$

Now, the only way this can be true is if  $q = 0.411$ . That is, we have the remarkable result that the value of  $1/X(x) \partial^2 X(x)/\partial x^2$  does not change when  $x$  is changed—it is a constant! In a similar way we can see that  $1/Y(y) \partial^2 Y(y)/\partial y^2$  is a constant too. The net result is that in this way we are able to separate

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} = -\frac{2m}{\hbar^2} E.$$

into two equations,

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} = -\frac{2m}{\hbar^2} E_x.$$

$$\frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} = -\frac{2m}{\hbar^2} E_y.$$

where  $E_x$  and  $E_y$  evidently are the contribution along each dimension to the total energy. This is a general result:

Whenever the wavefunction can be factored into a *product of wavefunctions* for separate dimensions, the energy is the *sum of energies* for these dimensions.

For the two dimensional particle in a box, this means the wavefunctions are

$$\psi(x, y)_{j,k} = \sqrt{\frac{4}{L_x L_y}} \sin(j\pi x/L_x) \sin(k\pi y/L_y),$$

the energies are

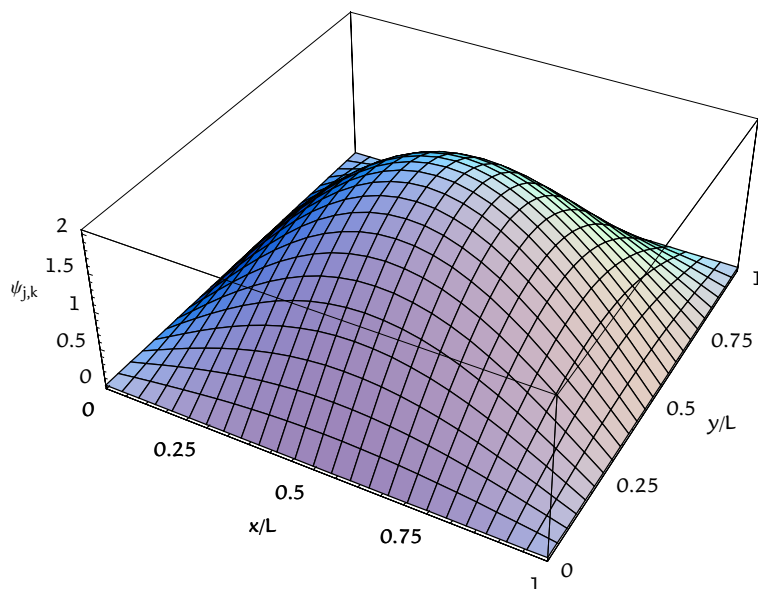
$$E_{j,k} = \frac{j^2 \hbar^2}{8m L_x^2} + \frac{k^2 \hbar^2}{8m L_y^2} = \frac{\hbar^2}{8m} \left( \frac{j^2}{L_x^2} + \frac{k^2}{L_y^2} \right),$$

and the zero point energy is

$$E_{1,1} = \frac{\hbar^2}{8m} \left( \frac{1}{L_x^2} + \frac{1}{L_y^2} \right).$$

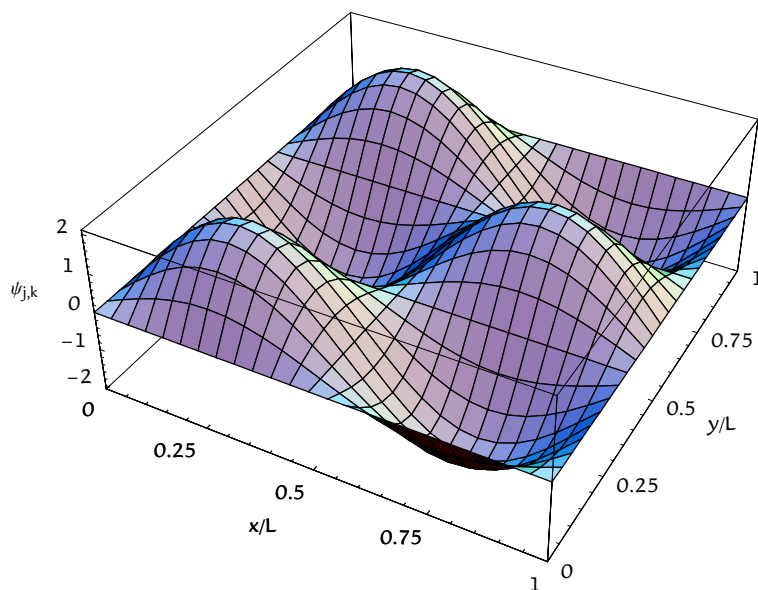
Write down the analogous expressions for a particle confined in three dimensions by infinite potential energy walls for zero potential energy inside the region.

Here is a surface plot of the lowest energy wavefunction,



Lowest energy wavefunction of a particle confined to a square, two-dimensional region.

and here is a plot of a higher energy wavefunction.



High energy wavefunction of a particle confined to a square, two-dimensional region.

Assume that the two surfaces are for an electron confined in a benzene ring, approximated as a two dimensional square of side  $4 \text{ \AA}$ . Calculate the wavelength of light needed to cause the electron wavefunction to change from the first, lowest-energy surface to the second, higher-energy surface. Answer:  $50 \text{ nm}$ . What region of the electromagnetic spectrum is this light?

Calculate the wavelength of light needed to cause the electron wavefunction to change from its lowest-energy surface to the surface consisting of one loop in one dimension and two loops in the other dimension. Answer: 200 nm. What region of the electromagnetic spectrum is this light?

This wavelength calculated in the previous problem is the longest wavelength light that such an electron can absorb. Based on this, what color do you expect benzene to be?

Calculate the zero point energy of free motion if one mole of  $\text{H}_2$  molecules confined in a container at STP. Assume the zero point energy is due to each molecule moving as a particle confined in a three dimensional box the size of the container. Answer:  $4 \times 10^{-19}$  kJ.

Why is the zero point energy of one mole of hydrogen molecules confined at STP so much less than the zero point energy of electrons confined in one mole of carotene molecules?