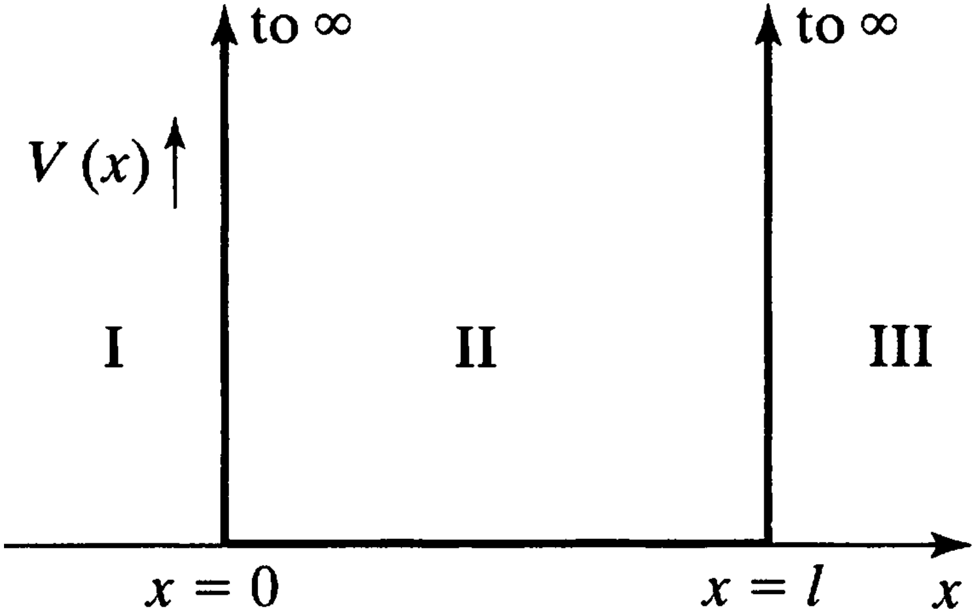
PARTICLE in a 1-DIMENSIONAL BOX

The aim is to find wave-function (and hence any info) and energy of a particle of mass m moving along the x axis and subject to a potential energy which is finite and constant in the interval $[0, l]$ and infinite outside the interval (a rough model for atoms and vibrating molecules; a better model for conjugate molecules)

$V(x) = V$
for $0 \leq x \leq l$

$V(x) = \infty$
for $x \leq 0$ and $x \geq l$



PARTICLE in a 1-DIMENSIONAL BOX

Since $V(x)$ does not depend on time, we look for solutions which are stationary states

time-independent Schrödinger equation
$$\hat{H}\psi(x) = \mathbb{E}\,\psi(x)$$

Making the Hamiltonian explicit $\rightarrow$
$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\,\psi(x) = \mathbb{E}\,\psi(x)$$

PARTICLE in a 1-DIMENSIONAL BOX

We have three regions. In **regions I and III** the potential energy is infinite

Exploiting $V(x) = \infty$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + (\infty - \mathbb{E})\psi(x) = 0$$

$\mathbb{E}$ can be neglected in comparison with ∞

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \infty\,\psi(x) = 0$$

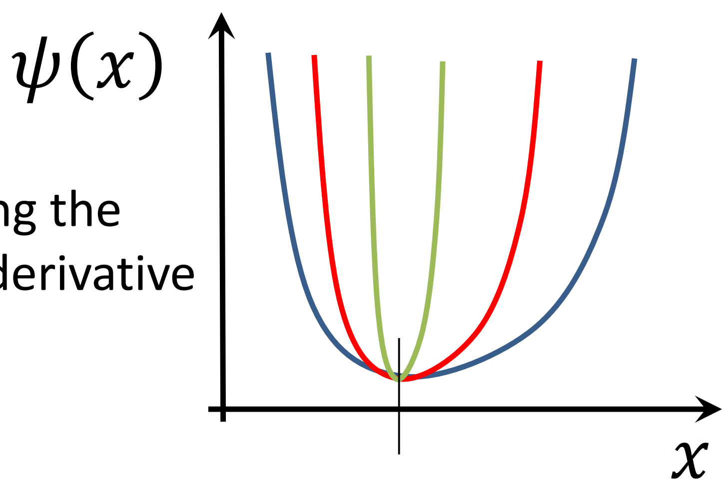
Exploiting $\psi(x)$

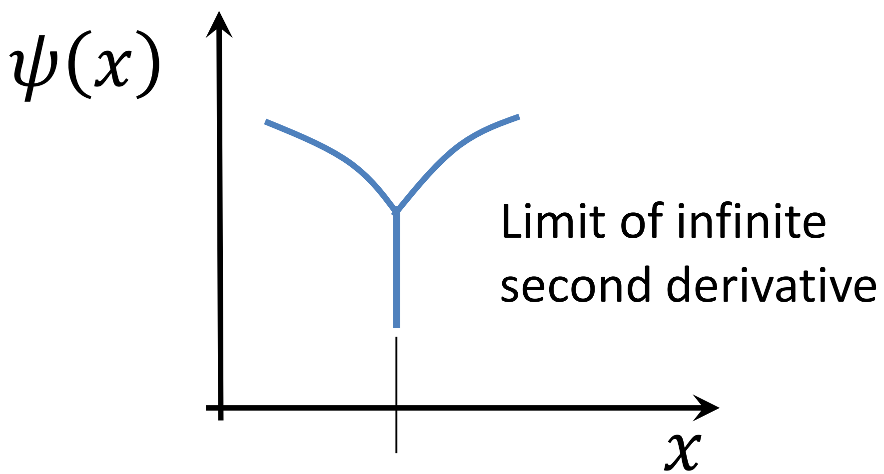
$$\psi(x) = \frac{1}{\infty}\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}$$

PARTICLE in a 1-DIMENSIONAL BOX

$$\psi(x) = \frac{1}{\infty}\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}$$

<u>The second derivative of $\psi(x)$ must not be infinite, otherwise $\psi(x)$ would not be a well-behaved function. In particular it would not be a single-value function</u>





Conclusion: **the particle cannot be found outside the box**

PARTICLE in a 1-DIMENSIONAL BOX

In **region II** the potential energy is constant, namely V

Exploiting $V(x) = V$ $$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + (V - \mathbb{E})\psi(x) = 0$$

For simplicity we can include V into $\mathbb{E}$. So, we set

$$E = \mathbb{E} - V$$

(E corresponds to the kinetic energy)

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} - E\,\psi(x) = 0$$

This is a linear homogeneous second-order differential equation with constant coefficients

PARTICLE in a 1-DIMENSIONAL BOX

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} - E\,\psi(x) = 0$$

By setting $\quad y = \psi(x) \qquad y'' = \dfrac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}$

The Schrödinger equation can be written shortly as

$$-\frac{\hbar^2}{2m}y'' - E\,y = 0$$

(We know how to find solutions!)

PARTICLE in a 1-DIMENSIONAL BOX

The solution is

$$\psi(x) = A\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right) + B\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right)$$

A and B are constant and can be determined by applying boundary conditions

PARTICLE in a 1-DIMENSIONAL BOX

By applying continuity at $x = 0$ we get $A = 0$

$$\psi(x) = B \sin\left(\frac{\sqrt{2mE}}{\hbar} x\right)$$

by applying continuity at $x = l$, we get

$$E = \frac{n^2\, h^2}{8\, m\, l^2} \qquad \text{with} \qquad n = 0, \pm 1, \pm 2, \pm 3, \ldots$$

Application of a boundary condition leads to conclude that **the energy is quantized** (not continuous)

PARTICLE in a 1-DIMENSIONAL BOX

Substituting E into the wave-function expression, we have

$$\psi(x) = B \sin\left(\frac{n\,\pi}{l}x\right) \qquad n = 0, \pm1, \pm2, \pm3, \ldots$$

Note that not all n values are allowed (for physical reasons)

1) The value $n = 0$ is not allowed because the wave-function would be 0 inside the box. So, it would be 0 everywhere in the monodimensional space (the particle would not exist!)

2) Positive and negative values of n lead to wave-functions differing only in the sign. The probability would be the same in both cases, so that they would represent the same state. One can choose only one sign (positive or negative does not matter; for simplicity positive values are chosen)

In conclusion $\qquad n = 1{,}2{,}3, \ldots$

PARTICLE in a 1-DIMENSIONAL BOX

$$E = \frac{n^2\, h^2}{8\, m\, l^2} \qquad\qquad n = 1, 2, 3, \ldots$$

Note that

1) There is a minimum value, greater than zero, for the energy of the particle (point zero energy)

2) The state of lowest energy is called the **ground state**. States with energies higher than the ground-state energy are **excited states**

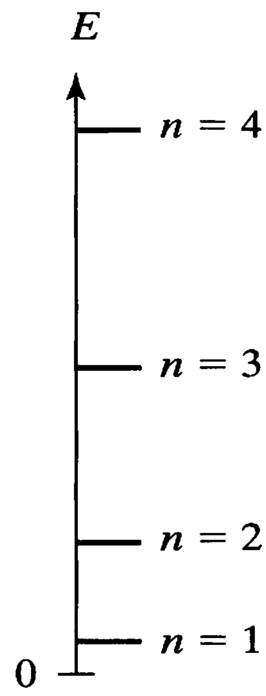
PARTICLE in a 1-DIMENSIONAL BOX

To complete the scenario, we need to normalize the wave-function

Inside the box
$$\boxed{\psi(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\,\pi}{l}x\right)}$$

Outside the box
$$\boxed{\psi(x) = 0}$$

Energy
$$\boxed{E = \frac{n^2\,h^2}{8\,m\,l^2} \qquad n = 1, 2, 3, \ldots}$$



n is called **quantum number**

PARTICLE in a 1-DIMENSIONAL BOX

The wave-function is zero at certain points; these points are called **nodes**

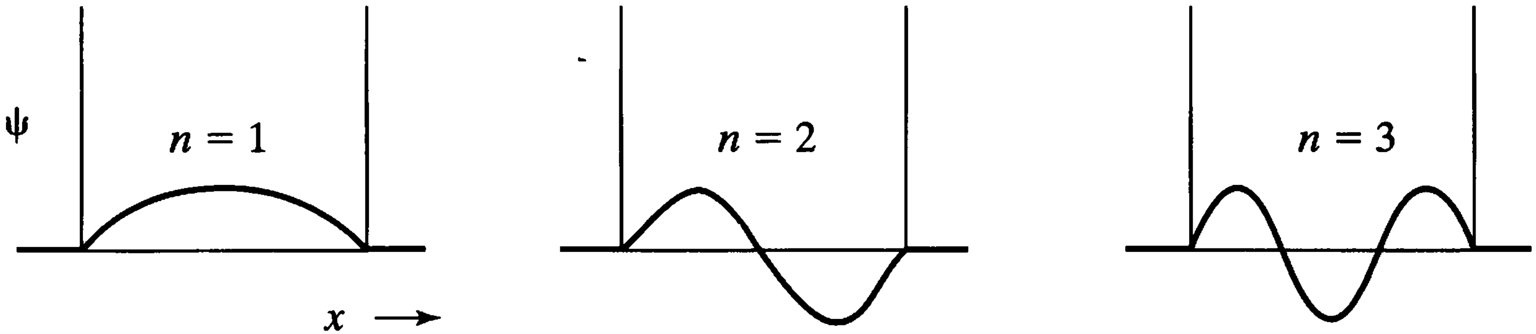


FIGURE 2.3 Graphs of ψ for the three lowest-energy particle-in-a-box states.

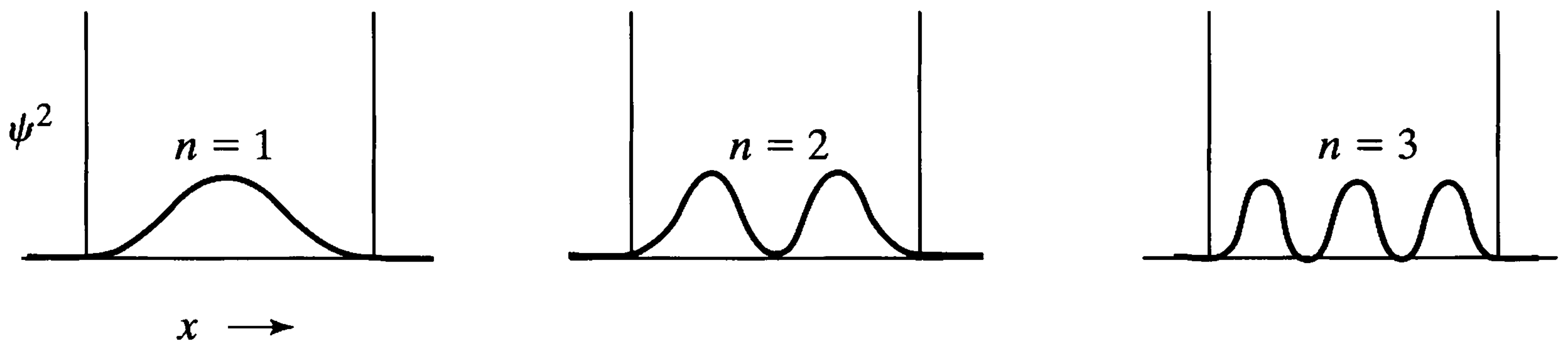


FIGURE 2.4 Graphs of $|\psi|^2$ for the lowest particle-in-a-box states.

PARTICLE in a 1-DIMENSIONAL BOX

Classically, it is equally likely to find the particle at any point in the box

Quantum mechanically, as we go to higher energy levels , the maxima and minima of probability come closer together, and the variations in probability along the length of the box ultimately become undetectable. **For high quantum numbers, we approach the result of classical mechanics**

This is a principle known as **Bohr correspondence principle**

NONINTERACTING PARTICLES AND SEPARATION OF VARIABLES

Suppose that a system is composed of the noninteracting particles 1 and 2. Let q_1 and q_2 symbolize the coordinates (x_1, y_1, z_1) and (x_2, y_2, z_2) of particles 1 and 2. Because the particles exert no forces on each other, the **classical-mechanical energy of the system is the sum of the energies of the two particles**: $E = E_1 + E_2 = T_1 + V_1 + T_2 + V_2$. This implies that the Hamiltonian operator is the sum of Hamiltonians for each particle:

$$\hat{H} = \hat{H}_1 + \hat{H}_2$$

The Schrödinger equation for the system is

$$\left(\hat{H}_1 + \hat{H}_2\right)\psi(q_1, q_2) = E\,\psi(q_1, q_2)$$

NONINTERACTING PARTICLES AND SEPARATION OF VARIABLES

We try a solution by separation of variables, setting

$$\psi(q_1, q_2) = F(q_1)\, G(q_2)$$

The solution is

Eigenvalue: $E = E_1 + E_2$

Eigeifunctions are obtained from solving the equations:

$$\hat{H}_1 F(q_1) = E_1\, F(q_1) \qquad \hat{H}_2 G(q_2) = E_2\, G(q_2)$$

(Lev.5 p. 125-126)

NONINTERACTING PARTICLES AND SEPARATION OF VARIABLES

This result is easily generalized to any number of noninteracting particles. For n such particles, we have

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \cdots + \hat{H}_n$$

$$\psi(q_1, q_2, \ldots, q_n) = G_1(q_1)G_2(q_2)\cdots G_n(q_n)$$

$$E = E_1 + E_2 + \cdots + E_n$$

$$\hat{H}_i G_i = E_i G_i\,, \qquad i = 1, 2, \ldots, n$$

For a system of noninteracting particles, the energy is the sum of the individual energies of each particle and the wave function is the product of wave functions for each particle

(Lev.5 p. 125-126)

PARTICLE in a 3-DIMENSIONAL BOX

The particle of mass m moves in a parallelepiped-shaped volume, where the potential energy is constant

$$V(x,y,z) = V \quad \text{for } 0 \le x \le a \quad 0 \le y \le b \quad 0 \le z \le c$$
$$V(x,y,z) = \infty \quad \text{otherwise}$$

In analogy with the 1-dimensional case, it can be shown that the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V(x,y,z)\,\psi = \mathbb{E}\,\psi$$

(Lev.5)

PARTICLE in a 3-DIMENSIONAL BOX

In analogy with the treatment of the 1-dimensional case, we can show that outside the box

$$\psi(x, y, z) = 0$$

while inside the box the time-independent Schrödinger equation can be written as

Setting

$E = \mathbb{E} - V$

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

We can use the *separation of variables* (slide 18)

$$\psi(x, y, z) = f(x)\, g(y)\, h(z)$$

(Lev.5)

PARTICLE in a 3-DIMENSIONAL BOX

The theorem reported at the slide 18 leads to

$$\frac{d^2 f(x)}{dx^2} + \frac{2m}{\hbar^2} E_x f(x) = 0$$

$$\frac{d^2 g(y)}{dy^2} + \frac{2m}{\hbar^2} E_y g(y) = 0, \qquad \frac{d^2 h(z)}{dz^2} + \frac{2m}{\hbar^2} E_z h(z) = 0$$

$$E_x + E_y + E_z = E$$

Boundary conditions: since the wave-function vanishes outside the box, continuity of ψ requires that it vanish on the walls of the box

(Lev.5)

PARTICLE in a 3-DIMENSIONAL BOX

The 3 equations are analogues to that found in the 1-dimensional case. Thus

The energy is
$$\boxed{E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)}$$

The wave-function is
$$\boxed{\psi(x, y, z) = \left(\frac{8}{abc}\right)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)}$$

$$n_x = 1,2,3,\ldots \quad n_y = 1,2,3,\ldots \quad n_z = 1,2,3,\ldots$$

Fot the ground state: $n_x = 1, n_y = 1, n_z = 1$

(Lev.5)

PARTICLE in a 3-DIMENSIONAL BOX

Since the single components of $f(x)$, $g(y)$ and $h(z)$ are normalized the ψ is also normalized

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi|^2\, dx\, dy\, dz = \int_0^a |f(x)|^2\, dx \int_0^b |g(y)|^2\, dy \int_0^c |h(z)|^2\, dz = 1$$

By setting $a = b = c$ (the box is a cube), the energy becomes

$$E = (h^2/8ma^2)(n_x^2 + n_y^2 + n_z^2)$$

Degeneracy appears! (it is introduced by symmetry)

(Lev.5)