

## Particle in a 1-D box

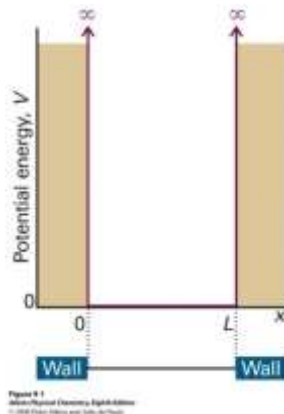


Figure 3.1: Particle in a 1-D box

### Free Particle inside

Inside the box, the particle experiences no potential energy,  $V(x) = 0$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E \psi \quad \text{or} \quad \frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad 0 \leq x \leq a$$

Also, outside the box the particle does not exist, i.e.  $\psi(x) = 0$ . Since  $\psi(x)$  tells us about the position, it should be a continuous function (we will discuss this more when we talk about the postulates)

$$\psi(0) = \psi(l) = 0$$

Solution,

$$\psi(x) = A \cos kx + B \sin kx \quad k = \sqrt{2mE}/\hbar^2$$

Boundary condition,  $\psi(0) = 0$  gives,

$$A = 0 \quad \text{and} \quad \psi(x) = B \sin kx$$

Boundary condition,  $\psi(l) = 0$

$$\psi(l) = B \sin kl = 0$$

$$kl = n\pi \quad n = 1, 2, 3 \dots$$

$$E_n = \frac{n^2 \hbar^2}{8m l^2} \quad n = 1, 2, 3 \dots$$

$$\psi_n(x) = B \sin \frac{n\pi x}{l} \quad n = 1, 2, 3 \dots$$

Question: Why  $n = 0$  is not a solution?

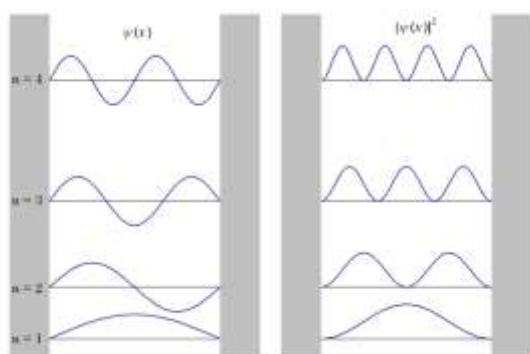


Figure 3.2:  $\psi(x)$  and  $\psi^*(x)\psi(x)$

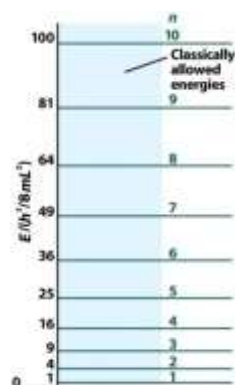


Figure 3.3: Energy levels

### The classic example of 1,3-butadiene

The PIB model can be applied to  $\pi$  electrons in conjugated systems. They are delocalized and are present over the entire chain. The  $\pi$  electrons can be thought of as particles in a box. Let the electrons not interact. Also, let's assume that butadiene is a linear molecule.

Bond length:  $2 C = C, 1 C - C, 2 r_{C-C} = (2 \times 135 + 154 + 2 \times 77) \text{ pm} = 578 \text{ pm}$

Energy:  $E_n = n^2 h^2 / 8m_e l^2$ .

Fill up the 4  $\pi$  electrons. Remember the Pauli exclusion principle.

Ground State: Two electrons each in  $n = 1$  and  $n = 2$  state

First excited state: Excitation from  $n = 2$  to  $n = 3$

$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{h^2}{8m_e l^2} (3^2 - 2^2) = 4.54 \times 10^4 \text{ cm}^{-1}$$

Observed:  $4.61 \times 10^4 \text{ cm}^{-1}$

### Normalization

The probability that the particle lies between 0 to  $l$  must be unity. After all the particle must be somewhere inside the box.

$$\int_0^a \psi^*(x)\psi(x)dx = 1$$

Using this fact we can determine  $B$ , the normalization constant (remember  $B$  is complex)

$$|B|^2 \int_0^a \sin^2 \frac{n\pi x}{l} dx = 1$$

$$\int_0^l \sin^2 \frac{n\pi x}{l} dx = \frac{l}{n\pi} \int_0^l \sin^2 z dz = \frac{l}{n\pi} \left( \frac{n\pi}{2} \right) = l/2$$

which gives,

$$B = \sqrt{\frac{2}{l}}$$

The normalized wavefunction is given by

$$\psi_n(x) = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \quad 0 \leq x \leq l \quad n = 1, 2, 3 \dots$$

Probability of finding the particle between  $x_1$  and  $x_2$

$$Prob(x_1 \leq x \leq x_2) = \int_{x_1}^{x_2} \psi^*(x)\psi(x)dx$$

### Bohr correspondence principle

Go to large values of  $n$  and see that the quantum mechanical result goes over to the classical limit.

## Orthogonality

All the eigenfunctions are orthogonal to each other

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j^* dx = 0$$

$$\int_0^l \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \sqrt{\frac{2}{l}} \sin \frac{m\pi x}{l} dx = 0$$

$$(\cos(A - B) - \cos(A + B)) = 2 \sin A \sin B$$

## Average quantities

### Average position

The average value of the position, by symmetry, should be the center of the box.

$$\langle x \rangle = \int_0^l x \psi^*(x)\psi(x)dx = \frac{2}{l} \int_0^l x \sin^2 \frac{n\pi x}{l} dx = \frac{2}{l} \frac{l^2}{4} = \frac{l}{2}$$

$$\left( \int x \sin^2 \alpha x dx = \frac{x^2}{4} - \frac{x \sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2} \right)$$

$$\langle x^2 \rangle = \frac{l^2}{3} - \frac{l^2}{2n^2\pi^2}$$

$$\left( \int x^2 \sin^2 \alpha x \, dx = \frac{x^3}{6} - \left( \frac{x^2}{4\alpha} - \frac{1}{8\alpha^3} \right) \sin 2\alpha x - \frac{x \cos 2\alpha x}{4\alpha^2} \right)$$

Variance

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{l^2}{12} - \frac{l^2}{2n^2\pi^2} = \left( \frac{l}{2\pi n} \right)^2 \left( \frac{\pi^2 n^2}{3} - 2 \right)$$

Standard deviation

$$\sigma_x = \frac{l}{2\pi n} \left( \frac{\pi^2 n^2}{3} - 2 \right)^{\frac{1}{2}}$$

### Average momentum

Particle travels equally in both directions  $+x$  and  $-x$ . Average momentum should be zero.

Since the operator for the momentum is a differential operator, where do we put it? Lets see the Schrödinger equation again

$$\hat{H}\psi_n(x) = E_n\psi_n(x)$$

Multiply the equation from the left by  $\psi_n^*$  and integrate over all space

$$\int \psi_n^*(x) \hat{H} \psi_n(x) \, dx = \int \psi_n^*(x) E_n \psi_n(x) \, dx = E_n \int \psi_n^*(x) \psi_n(x) \, dx = E_n$$

So in general sandwich the operator to get the average value

$$\langle p \rangle = \int_0^l \left[ \left( \frac{2}{l} \right)^{\frac{1}{2}} \sin \frac{n\pi x}{l} \right] \left( -i\hbar \frac{d}{dx} \right) \left[ \left( \frac{2}{l} \right)^{\frac{1}{2}} \sin \frac{n\pi x}{l} \right] dx$$

$$\langle p \rangle = 0$$

$$\langle p^2 \rangle = \frac{n^2 \pi^2 \hbar^2}{l^2}$$

$$\left( \int \sin^2 \alpha x \, dx = \frac{x}{2} - \frac{\sin 2\alpha x}{4\alpha} \right)$$

Also,  $\langle p^2 \rangle$  could have been calculated from the expression for energy.

So the standard deviation is

$$\sigma_p = \frac{n\pi\hbar}{l}$$

Variance is a measure of the spread in the values. In other words it is the uncertainty in the values.

Spread in momentum is inversely proportional to  $l$ , the length of the box.

Free particle:  $l = \infty$  ( $-\infty < x < \infty$ ). So no uncertainty in the measurement of momentum. Uncertainty in position is infinite.

$$\sigma_x \sigma_p = \frac{\hbar}{2} \left( \frac{\pi^2 n^2}{3} - 2 \right)^{\frac{1}{2}}$$

which gives the **Heisenberg Uncertainty** relation for the PIB  $\sigma_x \sigma_p > \hbar/2$

### Particle in a 3-D box

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E \psi(x, y, z) \quad \begin{cases} 0 \leq x \leq l_x \\ 0 \leq y \leq l_y \\ 0 \leq z \leq l_z \end{cases}$$

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

Boundary conditions:  $\psi$  vanishes at the boundaries of the cuboid

Use method of separation

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

Then,

$$E = E_x + E_y + E_z$$

Three separate identical equations need to be solved

$$\psi(x, y, z) = A_x A_y A_z \sin \frac{n_x \pi x}{l_x} \sin \frac{n_y \pi y}{l_y} \sin \frac{n_z \pi z}{l_z} \quad \begin{cases} n_x = 1, 2, 3 \dots \\ n_y = 1, 2, 3 \dots \\ n_z = 1, 2, 3 \dots \end{cases}$$

Normalization constant  $A_x A_y A_z = \left( \frac{8}{l_x l_y l_z} \right)^{\frac{1}{2}}$

$$E_{n_x n_y n_z} = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right)$$

### Degeneracy

What happens when the sides of the box are equal?  $l_x = l_y = l_z = l$

Lowest energy level is nondegenerate,  $E_{111} = \frac{3\hbar^2}{8ml^2}$

Next energy level is 3-fold degenerate,  $E_{211} = E_{121} = E_{112} = \frac{6\hbar^2}{8ml^2}$

Degeneracy is a result of the symmetry of the cube.

## Postulates of quantum mechanics

1) The wave function  $\psi(x)$  completely specifies the quantum mechanical system.  $\psi^*\psi dx$  is the probability that the particle lies between  $x$  and  $x + dx$ .

2) For every observable in classical mechanics, a corresponding operator exists in quantum mechanics. The operator is a linear, Hermitian operator.

3) In any measurement only eigenvalues are observed.  $\hat{A}\psi_n = a_n\psi_n$

4) Average value of the observable corresponding to operator  $\hat{A}$  is

$$\langle a \rangle = \int_{\text{all space}} \psi^* \hat{A} \psi dx$$

5) Time-dependent S. E.

$$\hat{H}\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

### Well-behaved wavefunctions

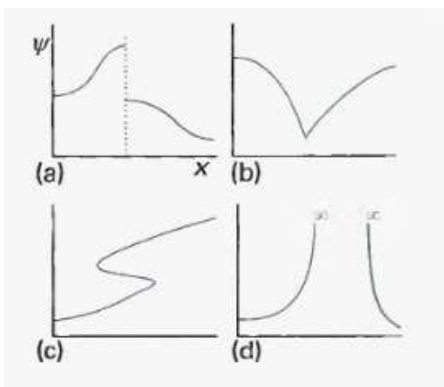


Figure 3.4: Unacceptable wavefunctions

Continuous, single-valued, slope continuous, finite - square integrable