Particle in a 1-D box

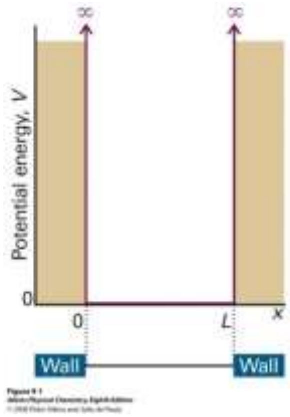

Figure 3.1: Particle in a 1-D box

Free Particle inside

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

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

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,

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

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

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

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

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

$$kl = n\pi \qquad n = 1, 2, 3 \ldots$$

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

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

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

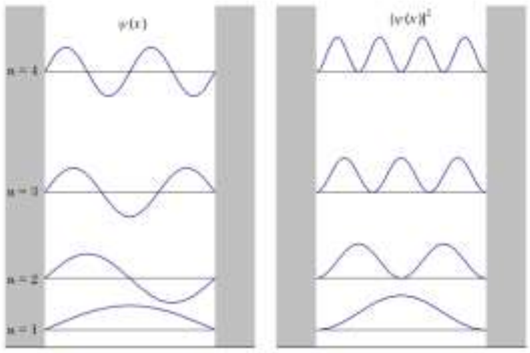

Figure 3.2: $\psi(x) \quad and \quad \psi^*(x)\psi(x)$

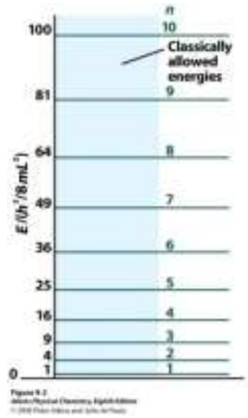

Figure 3.3: Energy levels

The classic example of 1,3-butadeiene

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

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

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

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 $n = 3$

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

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

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

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \qquad 0 \le x \le l \qquad n = 1, 2, 3 \ldots.}$$

Probability of finding the particle between x_1 and x_2

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

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.

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

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

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

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

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 ψ^* 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 $\quad \sigma_x \sigma_p > \hbar/2$

Particle in a 3-D box

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

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

Boundary conditions: ψ 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

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

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

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

Degeneracy

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

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

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

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

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

5) Time-dependent S. E.

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

Well-behaved wavefunctions

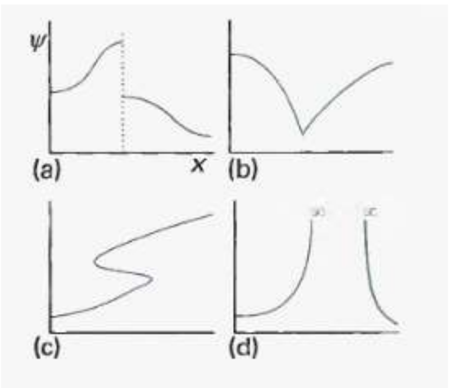

Figure 3.4: Unacceptable wavefunctions

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