## 3.4 Particle in a box

An electron in an atom can be considered to be trapped in a box of radius equal to the radius of the atom. To find the energy and wave function of the electron in an atom we will need to perform a three-dimensional calculation, but here we will model the situation as an one-dimensional box of size $a$. Let the potential energy be $U = 0$ inside the box and $U = \infty$ outside the box.

$$U = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le a \\ \infty & x > a. \end{cases} \tag{3.30}$$

This gives us three forms for the time-independent Schrödinger equation, Eq. 3.12 in the three domains. If the particle is in the domains $x < 0$ or $x > a$ its energy would be infinite. Therefore, we conclude that the particle will not be found outside the box. Therefore, the wave function will be zero outside the box.

$$\psi_E = \begin{cases} 0 & x < 0 \\ 0 & x > a. \end{cases} \tag{3.31}$$

The time-independent wave equation for $0 \le x \le a$ domain is obtained by setting $U(x) = 0$ in Eq. 3.12.

$$\frac{\partial^2 \psi_E}{\partial x^2} = -\frac{2mE}{\hbar^2}\,\psi_E. \tag{3.32}$$

This equation takes a simpler form if we set

$$k = \frac{\sqrt{2mE}}{\hbar}, \tag{3.33}$$

and write the equation usign $k$.

$$\frac{\partial^2 \psi_E}{\partial x^2} = -k^2 \psi_E. \tag{3.34}$$

We seek a solution of this equation with $\psi_E(0) = 0$ and $\psi_e(a) = 0$. The solution will be a sine function of $kx$.

$$\psi_E(x) = A \sin(kx). \tag{3.35}$$

It automatically satisfies $\psi_E(0) = 0$. To satisfy $\psi_E(a) = 0$, we demand

$$A \sin(ka) = 0. \tag{3.36}$$

Since $A \ne 0$, we must have

$$ka = n\pi, \quad n = 0, \pm 1, \pm 2, 3, \cdots . \tag{3.37}$$

Now, if $n = 0$ we will have $k = 0$, which would give $\psi_E(x) = 0$. That would mean the particle is not even in the box. Therefore, $n \ne 0$. Furthermore, Eq. 3.35 shows that the wave function is periodic in space of period $2\pi/k$, which would be the wavelength $\lambda$ of the wave.

$$\lambda = \frac{2\pi}{k}. \tag{3.38}$$

Since we would treat $\lambda > 0$, we would get $k > 0$. Labeling the allowed values of $k$ by an integer index $n$, the allowed values of $k$ will be

$$\boxed{k_n = \frac{n\pi}{a}, \quad n = 1, 2, 3, \cdots.} \tag{3.39}$$

Putting these values of $k_n$ in Eq. 3.33 we obtain the allowed values of energy, which will be labeled similarly with an index, $E_n$ to be:

$$k_n = \frac{\sqrt{2mE_n}}{\hbar} \quad \longrightarrow \quad E_n = \frac{\hbar^2 k_n^2}{2m}. \tag{3.40}$$

That is,

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad n = 1, 2, 3, \cdots. \tag{3.41}$$

We can write this more compactly as

$$\boxed{E_n = n^2 E_1, \quad n = 1, 2, 3, \cdots.} \tag{3.42}$$

with

$$\boxed{E_1 = \frac{\pi^2\hbar^2}{2ma^2} = \frac{h^2}{8ma^2}.} \tag{3.43}$$

The wave function $\psi$ is also labeled by the same index $n$:

$$\boxed{\psi_n(x) = A\sin(k_n x) = A\sin\left(\frac{n\pi x}{a}\right).} \tag{3.44}$$

The constant $A$ can be fixed by the normalization condition, which states that the probability of detecting the particle anywhere be 1. Since the wave function is zero outside the box, we will have the following integral relation.

$$\int_0^a \psi_n^* \psi_n dx = 1. \tag{3.45}$$

Therefore,

$$\int_0^a A^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = 1. \tag{3.46}$$

Taking $A^2$ outside the integral, writing the square of the sine function in terms of the double angle of cosine, and then performing the integral immediately gives

$$A^2 = \frac{2}{a}. \tag{3.47}$$

Therefore, we will have $A = \pm\sqrt{2/a}$. Since the wave function is always used as square we drop the minus sign and use only the positive $A$ here. This gives us the normalized wave function.

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}}\, \sin\left(\frac{n\pi x}{a}\right).} \tag{3.48}$$

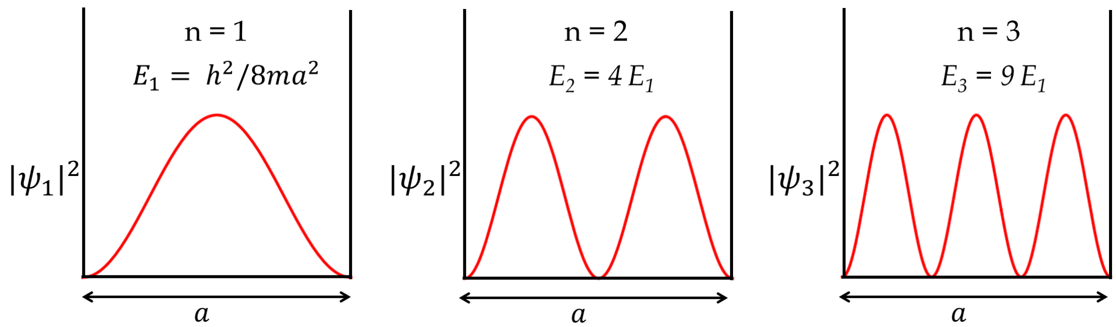


Figure 3.7: The probability densities of the three lowest energy states of a particle in the box. The horizontal axis is the $x$-axis here. Recall that the probability to find the particle between $x$ and $x + dx$ is given by $|\psi|^2 dx$.

Fig. 3.7 shows the probability densities corresponding to the three lowest energy states of a particle in a box.

The lowest energy state, called the **ground state**, has no nodes between the walls; that is, there is no place inside the box where the probability of finding the particle is zero. The ground state is also symmetric about the center of the box. The state with the next higher energy is the first excited state. The wave function of the first excited state has one node between the walls and hence the probability density has a value zero at one point at an inside point of the box. The second excited state has two nodes and each successively higher energy state has one more node. An important point of the energy levels of the particle in a box is the separation between the states varies as $n^2$ of the states. Thus, the separation of the energy levels $n = n_1$ and $n = n_2$ will be

$$E_{n_2} - E_{n_1} = \left(n_2^2 - n_1^2\right) E_1. \tag{3.49}$$

**Example 3.9. Energy levels of a particle in a box.** Consider an electron in a one-dimensional box of size equal to two times the Bohr radius, which is 52.9 pm. What will be the energies of the lowest three states?

**Solution.**

Let us first calcualte $E_1$ and then use $E_n = n^2 E_1$ to calculate the energies of other states.

$$E_1 = \frac{h^2}{8ma^2} = \frac{(6.63 \times 10^{-34}\text{J.s})^2}{8 \times 9.11 \times 10^{-31}\text{kg} \times (2 \times 52.9 \times 10^{-12}\text{m})^2} = 5.39 \times 10^{-18}\text{J}.$$

Therefore, $E_2$ and $E_3$ are

$$E_2 = 4E_1 = 2.16 \times 10^{-17}\text{J}, \qquad E_3 = 9E_1 = 4.85 \times 10^{-17}\text{J}.$$

**Example 3.10. Where is the particle in the box when in the ground state?** Suppose the particle is in the ground state, what is the probability that the particle will be on the left one-third of the box?

**Solution.**

The probability that the particle is between $x$ and $x + dx$ is given by

$$dP = |\psi_1(x)|^2 dx.$$

The left one-third of the box is between $x = 0$ and $x = a/3$. Therefore, we should integrate from $x = 0$ to $x = a/3$ to obtain the required probability.

$$\begin{aligned} P(\text{in left one-third of box}) &= \int_0^{a/3} \frac{2}{a}\sin^2\left(\frac{\pi x}{a}\right) dx = \frac{1}{a}\int_0^{a/3}\left[1 - \cos\left(\frac{2\pi x}{a}\right)\right] dx \\ &= \frac{1}{a}\left[\frac{a}{3} - \frac{a}{2\pi}\sin\left(\frac{2\pi}{3}\right)\right] = \frac{1}{3} - \frac{\sqrt{3}}{4\pi} \approx 0.21. \end{aligned}$$

The probability is not one-third. The particle in the ground state is more likely to be in the middle-third than the thirds near the walls. Question to student: What will be the probability for the particle to be in the middle third of the box when in the ground state? Note: no additional calculation is necessary. Ans: 0.58.

**Example 3.11. Where is the particle in the box when in the first excited state?** Suppose the particle is in the first excited state, what is the probability that the particle will be on the left one-third of the box?

**Solution.**

I have done the probability calculation for the ground state. In this problem we need to do the same steps for the first excited state $\psi_2$. The probability that the particle is between $x$ and $x + dx$ is given by

$$dP = |\psi_2(x)|^2 dx.$$

The left one-third of the box is between $x = 0$ and $x = a/3$. Therefore, we should integrate from $x = 0$ to $x = a/3$ to obtain the required probability.

$$\begin{aligned} P(\text{in left one-third of box}) &= \int_0^{a/3} \frac{2}{a}\sin^2\left(\frac{2\pi x}{a}\right) dx = \frac{1}{a}\int_0^{a/3}\left[1 - \cos\left(\frac{4\pi x}{a}\right)\right] dx \\ &= \frac{1}{a}\left[\frac{a}{3} - \frac{a}{4\pi}\sin\left(\frac{4\pi}{3}\right)\right] = \frac{1}{3} + \frac{\sqrt{3}}{4\pi} \approx 0.47. \end{aligned}$$

The probability is more than one-third. The particle in the first excited state is more likely to be in the left-third and the right-third than the middle third. Question to student: What will be the probability for the particle to be in the middle third of the box when in this state? Note: no additional calculation is necessary. Ans: 0.06.