

4.8: Other Properties of the Particle-in-a-Box

Now that we have mathematical expressions for the wavefunctions and energies for the particle-in-a-box, we can answer a number of interesting questions. The answers to these questions use quantum mechanics to predict some important and general properties for electrons, atoms, molecules, gases, liquids, and solids.

What is the lowest energy for an electron? The lowest energy level is E_1 , and it is important to recognize that this lowest energy is not zero. This finite (meaning neither zero nor infinite) energy is called the zero-point energy, and the motion associated with this energy is called the zero-point motion. Any system that is restricted to some region of space is said to be bound. The zero-point energy and motion are manifestations of the wave properties and the Heisenberg Uncertainty Principle, and are general properties of bound quantum mechanical systems. The position and momentum of the particle cannot be determined exactly. According to the Heisenberg Uncertainty Principle, the product of the uncertainties, i.e. standard deviations in these quantities, must be greater than or equal to $\hbar/2$. If the energy were zero, then the momentum would be exactly zero, which would violate the Heisenberg Uncertainty Principle unless the uncertainty in position were infinite. The system then would not be localized in space to any extent at all, which we will find to be true for the case of a free particle, which is not bound. The uncertainty in the position of a bound system is not infinite, so the uncertainty in the momentum cannot be zero, as it would be if the energy were zero.

Where is the electron?

Exercise 4.8.1

Use your solution to Exercise 4.8.15 to write a few sentences answering this question about the location of the electron. What insight do you gain from the graphs you made for the probability distribution at very large n compared to $n = 1$?

Exercise 4.8.2

Use the general form of the particle-in-a-box wavefunction $\sin(kx)$ for any n to find the mathematical expression for the position expectation value $\langle x \rangle$ for a box of length L . How does $\langle x \rangle$ depend on n ? Evaluate the integral.

Exercise 4.8.3

Calculate the probability of finding an electron at $L/2$ in an interval ranging from $\frac{L}{2} - \frac{L}{200}$ to $\frac{L}{2} + \frac{L}{200}$ for $n = 1$ and $n = 2$. Since the length of the interval, $L/100$, is small compared to L , you can get an approximate answer without integrating.

What is the momentum of an electron in the box?

The particle-in-a-box wavefunctions are not eigenfunctions of the momentum operator.

Exercise 4.8.4

Show that the particle-in-a-box wavefunctions are not eigenfunctions of the momentum operator.

Example 4.8.1

Even though the wavefunctions are not momentum eigenfunctions, we can calculate the expectation value for the momentum. Show that the expectation or average value for the momentum of an electron in the box is zero in every state.

Solution

First write the expectation value integral for the momentum. Then insert the expression for the wavefunction and evaluate the integral as shown here.

$$\langle P \rangle = \int_0^L \psi_n^*(x) \left(-i\hbar \frac{d}{dx} \right) \psi_n(x) dx \quad (4.8.1)$$

$$= \int_0^L \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \left(-i\hbar \frac{d}{dx}\right) \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) dx \quad (4.8.2)$$

$$= -i\hbar \left(\frac{2}{L}\right) \int_0^L \sin\left(\frac{n\pi x}{L}\right) \left(\frac{d}{dx}\right) \sin\left(\frac{n\pi x}{L}\right) dx \quad (4.8.3)$$

$$= -i\hbar \left(\frac{2}{L}\right) \left(\frac{n\pi}{L}\right) \int_0^L \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) dx \quad (4.8.4)$$

$$= 0 \quad (4.8.5)$$

It may seem that the electron does not have any momentum, which is not correct because we know the energy is never zero. In fact, the energy that we obtained for the particle-in-a-box is entirely kinetic energy because we set the potential energy at 0.

Since the kinetic energy is the momentum squared divided by twice the mass, it is easy to understand how the average momentum can be zero and the kinetic energy finite. It must be equally likely for the particle-in-a-box to have a momentum $-p$ as $+p$. The average of $+p$ and $-p$ is zero, yet p^2 and the average of p^2 are not zero.

The information that the particle is equally likely to have a momentum of $+p$ or $-p$ is contained in the wavefunction. The sine function is a representation of the two momentum eigenfunctions e^{ikx} and e^{-ikx} as shown by Exercise 4.8.5.

Exercise 4.8.5

Write the particle-in-a-box wavefunction as a normalized linear combination of the momentum eigenfunctions e^{ikx} and e^{-ikx} by using Euler's formula. Show that the momentum eigenvalues for these two functions are $p = +\hbar k$ and $-\hbar k$.

The interpretation of these results is physically interesting. The exponential wavefunctions in the linear combination for the sine function represent the two opposite directions in which the electron can move. One exponential term represents movement to the left and the other term represents movement to the right. The electrons are moving, they have kinetic energy and momentum, yet the average momentum is zero.

Does the fact that the average momentum of an electron is zero and the average position is $L/2$ violate the Heisenberg Uncertainty Principle? No, of course not, because the Heisenberg Uncertainty Principle pertains to the uncertainty in the momentum and in the position, not to the average values.

Quantitative values for these uncertainties can be obtained to compare with the limit set by the Heisenberg Uncertainty Principle for the product of the uncertainties in the momentum and position. First, we need a quantitative definition of uncertainty. Here, just like in experimental measurements, a good definition of uncertainty is the standard deviation or the root mean square deviation from the average. It can be shown by working Problem 6 at the end of this chapter that the standard deviation in the position of the particle-in-a-box is given by

$$\sigma_x = \frac{L}{2\pi n} \sqrt{\frac{\pi^2}{3} n^2 - 2} \quad (4.8.6)$$

and the standard deviation in the momentum by

$$\sigma_p = \frac{n\pi\hbar}{L} \quad (4.8.7)$$

Even for $n = 1$, the lowest value for n , σ_x is finite and proportional to L . As L increases the uncertainty in position of the electron increases. On the other hand, as L increases, σ_p decreases, but the product is never zero; and the uncertainty principle holds.

Exercise 4.8.6

Evaluate the product $\sigma_x \sigma_p$ for $n = 1$ and for general n . Is the product greater than $\hbar/2$ for all values of n and L as required by the Heisenberg Uncertainty Principle?

Are the eigenfunctions of the particle-in-a-box Hamiltonian orthogonal?

Two functions Ψ_A and Ψ_B are orthogonal if

$$\int_{\text{all space}} \psi_A^* \psi_B d\tau = 0 \quad (4.8.8)$$

In general, eigenfunctions of a quantum mechanical operator with different eigenvalues are orthogonal.

Exercise 4.8.7

Evaluate the integral $\int \psi_1^* \psi_3 dx$ and as many other pairs of particle-in-a-box eigenfunctions as you wish (use symmetry arguments whenever possible) and explain what the results say about orthogonality of the functions.

Exercise 4.8.8

What happens to the energy level spacing for a particle-in-a-box when mL^2 becomes much larger than \hbar^2 ? What does this result imply about the relevance of quantization of energy to baseballs in a box between the pitching mound and home plate? What implications does quantum mechanics have for the game of baseball in a world where \hbar is so large that baseballs exhibit quantum effects?

- Is quantization important for macroscopic objects?
- How can one determine the relative energies of wavefunctions by examination?

The first derivative of a function is the rate of change of the function, and the second derivative is the rate of change in the rate of change, also known as the curvature. A function with a large second derivative is changing very rapidly. Since the second derivative of the wavefunction occurs in the Hamiltonian operator that is used to calculate the energy by using the Schrödinger equation, a wavefunction that has sharper curvatures than another, i.e. larger second derivatives, should correspond to a state having a higher energy. A wavefunction with more nodes than another over the same region of space must have sharper curvatures and larger second derivatives, and therefore should correspond to a higher energy state.

Exercise 4.8.9

Identify a relationship between the number of nodes in a wavefunction and its energy by examining the graphs you made in Exercise 4.8.15. A node is the point where the amplitude passes through zero. What does the presence of many nodes mean about the shape of the wavefunction?

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