The Particle in a Box Model in Quantum Mechanics

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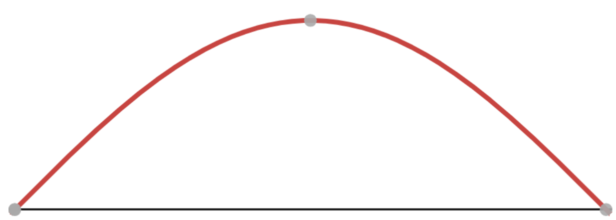
24th January, 2022

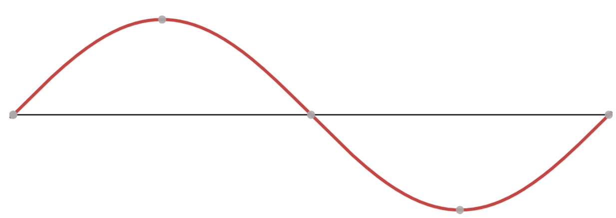
1 A heuristic derivation of the Energy levels of a one-dimensional Particle in a Box via Semiclassical Arguments:

While the energy levels of the stationary states of the Particle in a Box can be derived rigorously, by solving Schrödinger's Equation, they can also be derived via semiclassical arguments. Surprisingly, we get the same result either way!

If the particle in a box is in a stationary state, its wave function must be a standing wave, with nodes at the endpoints of the box. For example:



A standing wave with 2 nodes



A standing wave with 3 nodes

As can clearly be seen, if the wavelength of the standing wave is λ, then a standing wave with $n+1$ nodes must satisfy $\frac{n\lambda}{2} = L$, where L is the length of the box.

From de Broglie's Law, we know that $\lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$. Rearranging the terms, and using $\lambda = \frac{2L}{n}$ we get:

$$p_n = \frac{n\pi\hbar}{L} \tag{1}$$

Since, the potential energy in the box is 0, we can say that:

$$E_n = \frac{p_n^2}{2m} \tag{2}$$

Hence, we get:

$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}} \tag{3}$$

This is exactly the same expression we get after solving Schrödinger's Equation!

However, it is worth noting that this semiclassical argument does not give the correct values of all dynamical variables. Indeed, as we saw earlier, it predicts that $p_n = \frac{n\pi\hbar}{L}$, whereas actually, the stationary states of the particle in a box are not eigenvalues of the momentum operator ($\hat{p}$), i.e., the particle has no definite momentum. In fact, $\langle p \rangle = 0$.

2 A calculation of the Uncertainties in position and momentum for the stationary states of a Particle in a Box:

We know that the stationary states of a Particle in a Box are given by:

$$\Psi_n(x,t) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})e^{\frac{-iE_n t}{\hbar}} \tag{4}$$

where

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{5}$$

To calculate σ_x and σ_p, we will first calculate $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$, and $\langle p^2 \rangle$. We will then use the formulae:

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \tag{6}$$

$$\sigma_p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \tag{7}$$

Now,

$$\langle x \rangle = \langle \Psi_n | \hat{x}\Psi_n \rangle \tag{8}$$

We know that $\hat{x} = x$. Therefore,

$$\langle x \rangle = \langle \Psi_n | x\Psi_n \rangle = \int_{-\infty}^{\infty} \Psi_n^* x \Psi_n dx \tag{9}$$

$$\langle x \rangle = \frac{2}{L}\int_0^L x\sin^2(\frac{n\pi x}{L})dx \tag{10}$$

Therefore, on evaluating this integral, we get:

$$\langle x \rangle = \frac{L}{2} \tag{11}$$

Similarly, we can evaluate $\langle x^2 \rangle$, using the fact that $\hat{x^2} = \hat{x}^2 = x^2$.

$$\langle x^2 \rangle = \langle \Psi_n | \hat{x}^2 \Psi_n \rangle = \int_{-\infty}^{\infty} \Psi_n^* x^2 \Psi_n dx \tag{12}$$

$$\langle x^2 \rangle = \frac{2}{L}\int_0^L x^2\sin^2(\frac{n\pi x}{L})dx \tag{13}$$

On evaluating this integral, we get:

$$\langle x^2 \rangle = \frac{L^2}{6\pi^2 n^2}(2\pi^2 n^2 - 3) \tag{14}$$

Therefore, using $\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$, we get:

$$\sigma_x = \frac{L}{2\pi n}\sqrt{\frac{\pi^2 n^2 - 6}{3}} \tag{15}$$

Now, $\hat{p} = -i\hbar\frac{\partial}{\partial x}$. Therefore,

$$\langle p \rangle = \langle \Psi_n | \hat{p} \Psi_n \rangle = \int_{-\infty}^{\infty} \Psi_n^* (-i\hbar\frac{\partial \Psi_n}{\partial x})dx \tag{16}$$

$$\langle p \rangle = -\frac{2n\pi i}{\hbar L^2}\int_0^L \sin(\frac{n\pi x}{L})\cos(\frac{n\pi x}{L})dx \tag{17}$$

On evaluating this integral[1], we get:

$$\langle p \rangle = 0 \tag{18}$$

Note that these stationary states satisfy $\hat{H}\Psi_n = E_n\Psi_n$, where $\hat{H} = \frac{\hat{p}^2}{2m}$, and $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$. Therefore, we can say that:

$$\hat{p}^2\Psi_n = \frac{n^2\pi^2\hbar^2}{L^2}\Psi_n \tag{19}$$

Therefore, Ψ_n is an eigenfunction of $\hat{p}^2$. This is why the semiclassical method correctly predicts the Energies of the stationary states.

[1]It is possible to find $\langle p \rangle$ without evaluating this integral, by using Ehrenfest's Theorem, which states that $\langle p \rangle = m\frac{d\langle x \rangle}{dt}$. In a stationary state, $\langle x \rangle$ is constant, i.e. $\frac{d\langle x \rangle}{dt} = 0$. Therefore, in a stationary state, $\langle p \rangle = 0$.

Now,

$$\langle p^2\rangle = \langle\Psi_n|\hat{p^2}\Psi_n\rangle = \frac{n^2\pi^2\hbar^2}{L^2}\langle\Psi_n|\Psi_n\rangle = \frac{n^2\pi^2\hbar^2}{L^2} \tag{20}$$

Therefore, using $\sigma_p = \sqrt{\langle p^2\rangle - \langle p\rangle^2}$, we get:

$$\sigma_p = \frac{n\pi\hbar}{L} \tag{21}$$

Identifying σ_x and σ_p with the uncertainties Δx and Δp and multiplying them, we get:

$$\boxed{\Delta x\Delta p = \frac{\hbar}{2}\sqrt{\frac{\pi^2 n^2 - 6}{3}}} \tag{22}$$

From this expression, it is easily verified that $\Delta x\Delta p \geq \frac{\hbar}{2}$, i.e., Heisenberg's Uncertainty Principle is followed.

3 Zero Point Energy, and how it arises from the Uncertainty Principle:

The Energies of the Stationary States of the Particle in a Box are given by:

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{23}$$

where n is a **positive** integer. This implies, that even in the state of lowest energy (known as the Ground State), the energy of the particle is non-zero. The minimum energy that the system can possess[2] is known as the Zero Point Energy, and for the Particle in a Box, it is given by:

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} \tag{24}$$

Classically, however, the minimum energy that a particle could posses would be zero (when the particle is at rest). The existence of zero point energy in Quantum Mechanics can be explained by Heisenberg's Uncertainty Principle.

If the particle were at rest, it's momentum would be zero (the particle would be in an eigenstate of momentum with eigenvalue 0). Therefore, the uncertainty in the particle's momentum would also be zero. Hence, by Heisenberg's Uncertainty Principle, the uncertainty in the position of the particle should tend to ∞ in this state. However, since the particle is bound inside a box, the maximum uncertainty of the particle must be on the order of the size of the box, which is

[2] If the particle exists in a linear combination of stationary states, then it is no longer in a state of definite Energy, and the Energy of the particle is identified with the expectation value of the Energy ($\langle E\rangle$). Since every measurement of E will return one of the allowed energies E_n, and since $E_n \geq E_1$, $\langle E\rangle \geq E_1$.

finite. Therefore, the particle cannot be at rest, which means that the particle cannot have zero energy, like it could classically.

To make this quantitative, note that:

$$\langle E \rangle = \frac{\langle p^2 \rangle}{2m} \tag{25}$$

Now, $\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$. Therefore, $\langle p^2 \rangle = \Delta p^2 + \langle p \rangle^2 \geq \Delta p^2$. Now, let us choose our coordinate system such that the origin lies at the centre of the box. So $-\frac{L}{2} \leq x \leq \frac{L}{2}$. That is, $x^2 \leq \frac{L^2}{4}$, and therefore, $\langle x^2 \rangle \leq \frac{L^2}{4}$. Now $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \leq \sqrt{\langle x^2 \rangle} \leq \frac{L}{2}$.

Now, according to Heisenberg's Uncertainty Principle, $\Delta x \Delta p \geq \frac{\hbar}{2}$. Therefore,

$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq \frac{\hbar}{L} \tag{26}$$

and

$$\langle E \rangle = \frac{\langle p^2 \rangle}{2m} \geq \frac{\Delta p^2}{2m} \geq \frac{\hbar^2}{2mL^2} \tag{27}$$

Therefore[3],

$$\boxed{\langle E \rangle \geq \frac{\hbar^2}{2mL^2}} \tag{28}$$

Which means that the particle cannot exist in a state with 0 energy.

[3] It is seen that the minimum Energy derived via Heisenberg's Uncertainty Principle ($\frac{\hbar^2}{2mL^2}$) is less than the actual zero point energy of the particle ($\frac{\pi^2\hbar^2}{2mL^2}$). This is because, in the ground state of the particle, the Wave Function is not a Gaussian Wave Packet, i.e., equality does not occur in Heisenberg's Uncertainty Principle. There are certain systems (such as the Harmonic Oscillator), where the ground state wave function **is** a Gaussian Wave Packet, and Heisenberg's Uncertainty Principle can be used to exactly determine the zero point energy of the system, and not just a lower bound on it.