Particle in a Box

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Time Dependent Schroedinger's equation

Schroedinger proposed that Energy and Momentum should be treated as Operators. He also proposed

$$P_x = -i\hbar\frac{\partial}{\partial x}$$

$$E = i\hbar\frac{\partial}{\partial t}$$

He also introduced a mysterious object $\psi(x, t)$, which he called wave function. And claimed that the dynamics of $\psi(x, t)$ is given by the equation

$$i\hbar\frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x)\psi(x, t).$$

What this wave function describes *he had no idea*.

Max Born gave the correct interpretation of what $\psi(x, t)$ means. He said that $|\psi(x, t)|^2 dx$ is the probability of finding the electron between x and $x + dx$.

Time Dependent Schroedinger's equation

Sum of all probabilities should add upto 1. Hence we have the constraint

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 1.$$

Born's interpretation demands that the wave function should be normalized.

In Schroedinger's viewpoint, all physical observables are represented by Operators. Given an operator O, we can calculate its expectation value

$$\langle O \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) O \psi(x,t) dx.$$

Time Dependent Schroedinger's equation

If we take an ensemble of atoms containing electrons with wavefunctions $\psi(x, t)$ and measure the observable O, then the measured value will be close to the expectation value calculate above.

In addition to the calculation of the expectation value, we can also calculate the uncertainty

$$\Delta O = \sqrt{\langle O^2 \rangle - \langle O \rangle^2},$$

where

$$\langle O^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) O^2 \psi(x, t) dx.$$

Time Independent Schroedinger's equation

An important reason for developing Quantum Mechanics is to explain the Spectra seen in atoms.

Bohr explained this feature saying that, in an atom, an electron can occupy only some definite, fixed energy states.

Using Schroedinger's equation, we can calculate both the values of energy for these states and also the wave functions for them.

If the energy E is fixed for these special states, the corresponding wave function should satisfy the equation

$$i\hbar\frac{\partial\psi_E(x,t)}{\partial t} = E\psi_E(x,t).$$

Sovling this we get

$$\psi_E(x,t) = \psi_E(x)\exp\left[-i\frac{Et}{\hbar}\right].$$

Time Indepednent Schroedinger's equation

If we substitute this in time dependent Schroedinger's equation, we get the
time independent Schroedinger's equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi_E(x)}{\partial x^2} + V(x)\psi_E(x) = E\psi_E(x).$$

Solutions to this equation, $\psi_E(x)$ are called energy eigenstates, with
energy eigenvalue E.

They are also called stationary states because $|\psi_E(x,t)|^2 = |\psi_E(x)|^2$.
Once the electron is in an energy eigenstate (or a stationary state) it will
remain there forever, as long as the potential remains unchanged.

In Quantum Mechanics, a very standard problem we try to solve is to find
the energy eigenvalues and energy eigenstates for any given potential.

Particle in an Infinite Potential Well

It is the simplest non-trivial problem in quantum mechanics. In one dimension the motion of the particle is bound an infinite potential well. Mathematically, the potential is defined by

$$
\begin{aligned}
V(x) &= 0 \text{ for } 0 < x < L \\
&= \infty \text{ for all other x}
\end{aligned}
$$
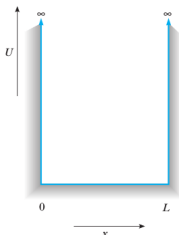
It is also called particle in a box problem.

Schroedinger's Equation for a Particle in a Box

- We want to solve the time independent Schroedinger's equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x),$$

  for the potential of the infinite potential well.

- We look for solutions with finite value of energy. Hence, the only allowed solution for $x \leq 0$ and $x \geq L$ is $\psi(x) = 0$.

- For $0 < x < L$, the Schroedinger's equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x),$$

- This is better written as

$$\begin{aligned}\frac{d^2\psi(x)}{dx^2} &= -\frac{2mE}{\hbar^2}\psi(x) \\ &= -k^2\psi(x),\end{aligned}$$

  where we defined $k^2 = 2mE/\hbar^2$ or $E = \hbar^2 k^2/2m$.

Conditions on the Wavefunctions for a Particle in a BoX

- This is a very well known differential equation. The solutions can be written as the linear combinations of either $\exp(ikx)$ and $\exp(-ikx)$ or $\cos(kx)$ and $\sin(kx)$.

- We choose the solution in the form of the trigonometric functions, because it is easier to impose the boundary conditions in that form.

- The potential undergoes an infinite change at the points $x = 0$ and at $x = L$. From the Schroeding's equation, we see that the second derivative $d^2\psi/dx^2$ at these points must also be infinite.

- This is in turn leads to the conclusion that, at $x = 0$ and at $x = L$, the first derivative $d\psi/dx$ has a disconuity. That means that $\psi(x)$ is continuous at $x = 0$ and at $x = L$ but it has a kink.

- We argued before that for x outside the box, $\psi(x) = 0$ (no finite energy solution at points where the potential diverges).

- The above arguments leads to the conclusion that $\psi(x) = 0$ at $x = 0$ and at $x = L$.

Quantization condition for a Particle in a Box

- Given the above conditions, the most general solution for the Schroedinger's equation is $\psi(x) = N \sin(kx)$. It automatically vanishes at $x = 0$ and we demand that it should vanish at $x = L$.

- This leads to the quantization condition $kL = n\pi$, where n is a positive integer ($n = 1, 2, 3, ...$).

- Substituting this in the expression for energy, we get

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{8mL^2}.$$

Energy is QUANTIZED!

- The particle is allowed to take only discrete values of energy. And if it makes transitions between them, the emitted energy will have some pre-determined values.

- The situation is very similar to what was enocuntered in Bohr's model of hydrogen atom.

Energy Eigenstates and Eigenvalues

- Demanding that the energy eigenstates should be normalized, that is

$$\int_{-\infty}^{+\infty} |\phi_n(x)|^2 dx = \int_0^L N^2 \sin^2\left(\frac{n\pi x}{L}\right) = 1$$

gives the normalization constant $N = \sqrt{2/L}$. It is the same for all the states. It is independent of n in this problem.

- The first few energy eigenstates and their corresponding eigenvalues are
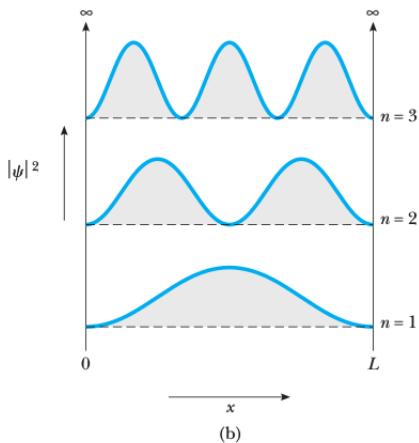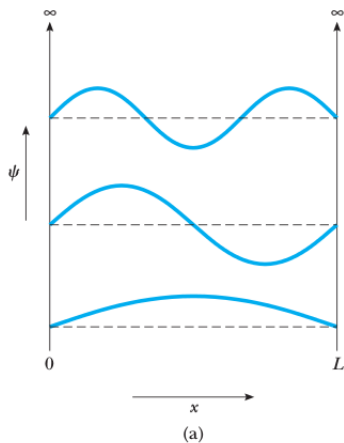
$$\phi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right), \ E_1 = \frac{\pi^2\hbar^2}{2mL^2}$$

$$\phi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right), \ E_2 = \frac{4\pi^2\hbar^2}{2mL^2} \ \cdots$$

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \ E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

- **Notation**: A general wavefunction is denoted by $\psi(x)$. In any given problem, the energy eigenstates are denoted by $\phi_n(x)$.

Graphs of Energy Eigenstates

(a)

(b)

Symmetry Properties of Energy Eigenstates

- The states with odd n are even under the transformation $x \rightarrow (L - x)$, whereas the states with even n are odd under this transformation. In particular the ground state is even and so is the potential.
- **Theorem**: If the potential has a symmetry, the lowest energy state (called the ground state) has the same symmetry.
- The above symmetry is called **Parity** and it is one of the most important symmetries of nature. It dictates which atomic transitions are allowed and which are forbidden.
- It was a shock to many people when it was experimentally demonstrated that beta decay does not have this symmetry.
- The ground state has no nodes, that is $\phi_1(x) \neq 0$ anywhere within the well. The first excited state has one node, the second excited state has two nodes etc.
- This is a general feature of all problems where Parity is a symmetry. The eigenstates alternate between even and odd and the integer characterizing the eigenstate also gives the number of nodes.

General Properties of Energy Eigenstates

- In classical mechanics, if the potential is zero, then the lowest energy is zero. But here the lowest allowed energy is non-zero!

- Because the height of the potential is taken to be infinite, we have an infinite number of bound states. In most cases, the height (or depth) of the potential well is finite. In such cases, we will have only a limited number of bound states.

- States with very large n behave essentially like classical particles.

- The energy eigenstates are orthogonal to one another.

$$\int_{-\infty}^{+\infty} \phi_m^*(x)\phi_n(x)dx = \int_0^L \sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx = 0 \text{ if } m \neq n.$$

- The energy eigenstates form an orthonormal basis set. Any arbitrary wavefunction for a particle in a box can be written as

$$\psi(x) = \sum_n c_n\phi_n(x).$$

Meaning of Eigenvalues and Eigenstates

- Suppose the particle is in the ground state of the infinite potential well.

$$\psi(x, t) = \phi_1(x) \exp\left(\frac{-iE_1 t}{\hbar}\right).$$

  I do an experiment where I measure the energy of the particle.

- What result do I get? Since the particle is in the ground state, my measurement gives the result E_1.

- What happens to the particle, after I have made the measurement? In this case, **nothing**.

- Why? An energy measurement makes the wave function **collapse** into one of the energy eigenstates. Since the original state is an energy eigenstate, it remains in the same state after the energy measurement.

Meaning of Eigenvalues and Eigenstates

- Once again I start with the particle in the ground state, but this time I measure its momentum.

- The ground state can be written as the linear combination linear combination

$$\phi_1(x) = \sqrt{2/L}\sin(\pi x/L) = \frac{\sqrt{2/L}}{2i}\left[\exp(i\pi x/L) - \exp(-i\pi x/L)\right].$$

- So the ground state (and every other state in this problem) are linear combinations of two momentum states $\hbar k$ and $-\hbar k$. So the momentum measurement gives one of these two values as a result.

- Suppose we got the answer $\hbar k$. The momentum measurement makes the ground state collapse into a momentum eigenstate. If we immediately make another momentum measurement, we get the result $\hbar k$ again.

Meaning of Eigenvalues and Eigenstates

- Suppose we wait for a bit and then make the momentum measurement. Now it is possible to get either of the results $\hbar k$ or $-\hbar k$.

- Why is that? Did not our first momentum measurement force the particle into a momentum eigenstate?

- Yes. But then we left the particle alone. The only influence on the particle is only the potential. It is this potential and the kinetic energy which guide the further time evolution of the wave function.

- Our first momentum measurement has forced the particle into one of the two momentum eigenstates of the ground state. Later, this state becomes the usual ground state. When there is no external influence on the particle, the wave function of the particle should be either an energy eignestate or a linear combination of energy eigenstates.

- Here the momentum measurement never took it out of the ground state. Hence at later times, the wave function is the general ground state, not just the $\hbar k$ part of the ground state.