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Modern physics

2. The Schrödinger equation

Outline

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2.1. Conceptual consequences of particles as waves

Some serious difficulties arise when we think carefully about de Broglie's hypothesis. From the classical point of view, an electron which is a particle, should have a well-defined path described by a position vector $\vec{\mathbf{r}}(t)$

This leads to an apparently paradoxical result, as far as the transmission of electrons through a pair of slits is considered.

A classical interference pattern is produced on the screen when one part of a wave passes through one slit and another part through the other slit.
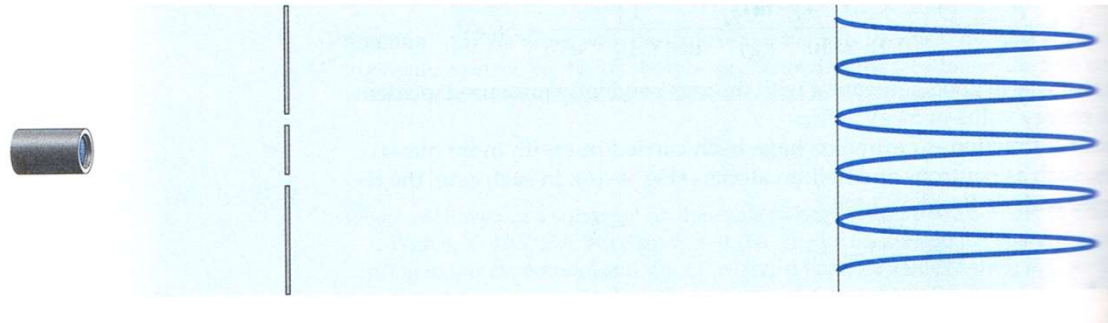
But a particle with a well-defined path passes through only one slit or the other.

2.1. Conceptual consequences of particles as waves

The observation of two-slit interference with electrons is not connected with interference between different electrons. We can reduce the number of electrons that pass through the slits per unit time to the point where it is clear that the effect is due to the passage of one electron after another.
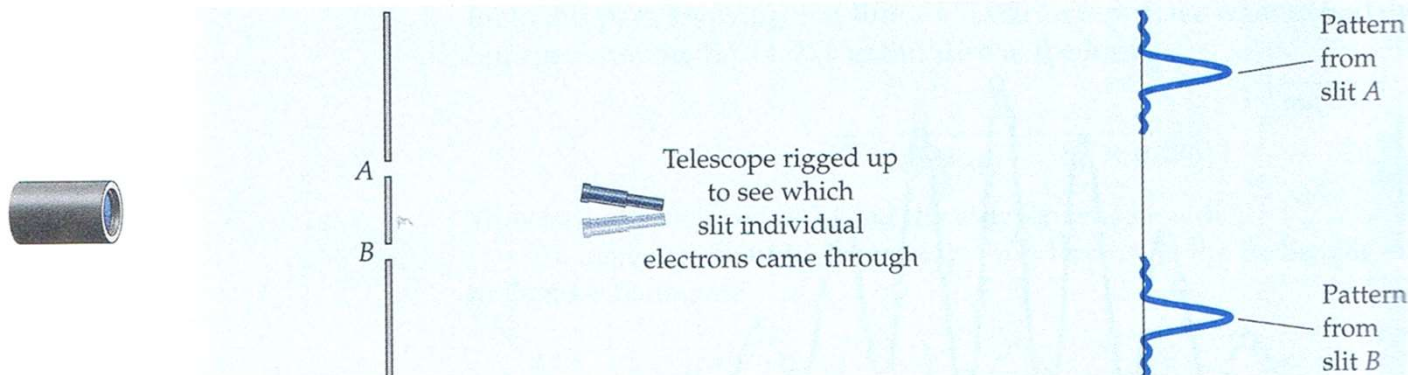

8 electrons

270 electrons

2000 electrons
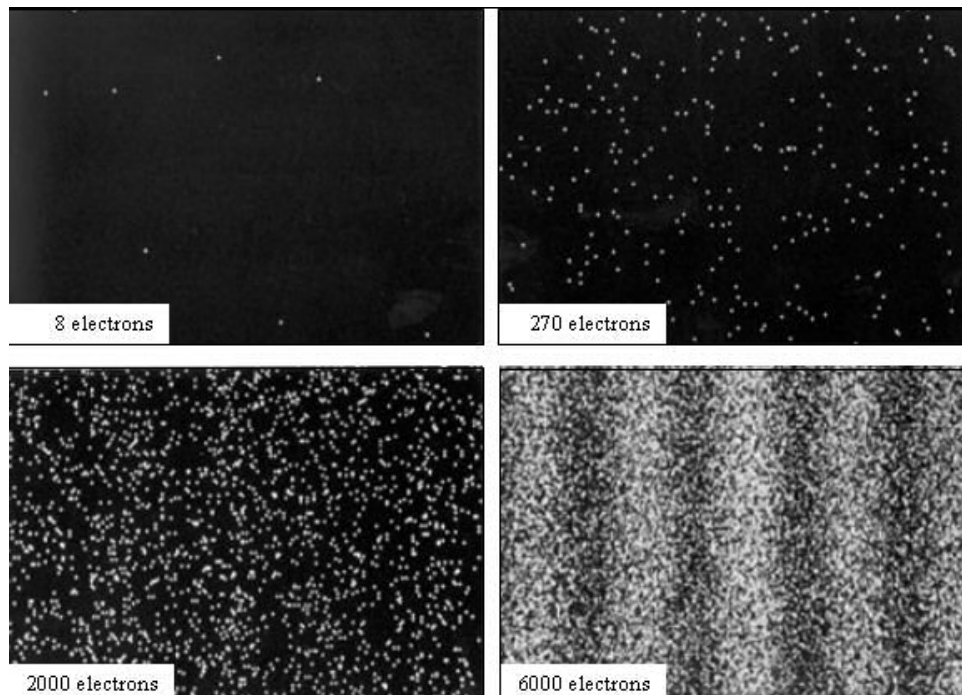
6000 electrons

Individual electrons coming at a rate of 1000 per second (which, at the energies the electrons posses, corresponds to spatial separation of 150 km) nevertheless create an interference pattern

The photos illustrate how the pattern is built up as the number of electrons increases

2.1. Conceptual consequences of particles as waves

A further troubling aspect enters when we employ a detection apparatus that can tell when an electron passes through one slit or the other. We could even tell, by measuring the electron's precise direction of travel, which slit it was going to pass through and, in anticipation, shut the other slit. But when we do this, *the interference effect disappears.*

Somehow, the measurement itself has decided whether the electron has behaved like a particle or like a wave

If a monitor identifies which slit any individual electron passes through, the pattern is a sum of the pattern due to electron passing through single slits

2.1. Conceptual consequences of particles as waves

Conceptual difficulties arise from the idea that **radiation** has **particlelike** properties while **matter** has wavelike **properties**. When photons or electrons are sent through a two-slit system at such a slow rate that their arrivals are separated by very long times, they nevertheless gradually give rise to a characteristic wavelike interference pattern. Any particular „hit" on the screen by a photon or electron appears to be random, but the result of the accumulation of „hits" produces the pattern

In the classical limit, there are no photons. We have classical electromagnetic wave that follows from Maxwell's equations.

$$\nabla^2 \vec{\mathbf{E}} = \mu_o \varepsilon_o \frac{\partial^2 \vec{\mathbf{E}}}{\partial t^2}$$

This wave can be fully described by specifying the electric field it contains.

The collective effect of many photons is described by an electric field $\vec{\mathbf{E}}(\vec{\mathbf{r}}, t)$

How is the classical interference pattern formed?

The interference pattern appears on the screen because there is an electric field $\vec{\mathbf{E}}_1$ associated with the part of the wave coming through slit 1 and an electric field $\vec{\mathbf{E}}_2$ associated with the part of the wave coming through slit 2, and the net classical field on the far side of the slits will have the form suggested by the principle of superposition

$$\vec{\mathbf{E}}(\vec{\mathbf{r}},t) = \vec{\mathbf{E}}_1(\vec{\mathbf{r}},t) + \vec{\mathbf{E}}_2(\vec{\mathbf{r}},t)$$

The pattern on the screen is an *intensity* pattern:

$$I \propto \vec{\mathbf{E}}(\vec{\mathbf{r}},t)^2 = (\vec{\mathbf{E}}_1(\vec{\mathbf{r}},t) + \vec{\mathbf{E}}_2(\vec{\mathbf{r}},t))^2$$

$2\vec{\mathbf{E}}_1(\vec{\mathbf{r}},t) \circ \vec{\mathbf{E}}_2(\vec{\mathbf{r}},t)$ is the interference term

Because of vector character of electric fields, they sometimes reinforce and sometimes cancel each other

Interference of single photons?

The intensity of the wave is proportional to the square of the field $\vec{\mathbf{E}}(\vec{\mathbf{r}},t)$ which is in turn proportional to the number of photons, N, at point $\vec{\mathbf{r}}(t)$ at time t.

When the intensity of the light shining on the slits decreases, N decreases as well until we are dealing with one photon at a time. Even single photons carry with them the interference properties characteristic of N photons.

Each single photon is associated with an electric field $\vec{\mathbf{e}}(\vec{\mathbf{r}},t)$ that, like the ordinary electric field obeys the rules of superposition and solves the linear equation.

Interference of single photons?

The electric field at the screen due to a single photon in a two-slit experiment has a form

$$\vec{e}(\vec{r},t) = \vec{e}_1(\vec{r},t) + \vec{e}_2(\vec{r},t)$$

$\vec{e}_1(\vec{r},t)$ is the field due to a photon that came through slit 1 with slit 2 closed

$\vec{e}_2(\vec{r},t)$ is the field due to a photon that came through slit 2 with slit 1 closed

The quantum analog to the classical intensity is

$$I \propto \left[\vec{e}(\vec{r},t)\right]^2 = \left[\vec{e}_1(\vec{r},t) + \vec{e}_2(\vec{r},t)\right]^2$$

Interference of single photons?

Since photons are indivisible, we cannot speak of some fraction of a photon coming through one slit or the other!

Therefore, I in the formula:

$$I \propto \left[\vec{\mathbf{e}}(\vec{\mathbf{r}},t)\right]^2 = \left[\vec{\mathbf{e}}_1(\vec{\mathbf{r}},t) + \vec{\mathbf{e}}_2(\vec{\mathbf{r}},t)\right]^2$$

represents a probability distribution function while:

$$\left[\vec{\mathbf{e}}(\vec{\mathbf{r}},t)\right]^2 d^3\vec{\mathbf{r}}$$

is proportional to the **probability** that a photon can be found in the box of size $d^3\vec{\mathbf{r}}$ around the point $\vec{\mathbf{r}}$

Matter waves

For electrons and other material particles there is no classical field (as for photons)

We assume that associated with each electron is a **wave function** $\psi(\vec{r}, t)$ that must obey some linear equation.

This is **Schrödinger equation**.

Linearity implies that if $\psi_1(\vec{r}, t)$ and $\psi_2(\vec{r}, t)$ are solutions of Schrödinger equation, then so is:

$$\psi(\vec{r}, t) = A\psi_1(\vec{r}, t) + B\psi_2(\vec{r}, t)$$

where A and B are arbitrary complex constants

Interference of matter waves

Thus if $A\psi_1(\vec{\mathbf{r}},t)$ is the wave function for an electron that came through slit 1 and $B\psi_2(\vec{\mathbf{r}},t)$ is the wave function for an electron that came through slit 2, then the wave function for the electron at the screen on the far side of the slits is the sum of these two wave functions. The square of the sum, which is associated with the probability for finding an electron, includes interference terms needed for a proper description of the passage of an individual electron through a two-slit system.

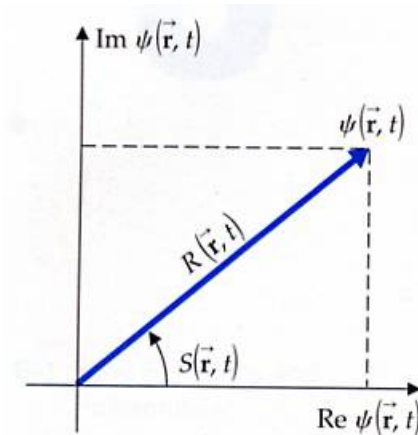The wave function $\psi(\vec{\mathbf{r}},t)$ can be a **complex** function

$$\psi(\vec{\mathbf{r}},t) = R(\vec{\mathbf{r}},t)\exp\!\left[iS(\vec{\mathbf{r}},t)\right]$$

where $R(\vec{\mathbf{r}},t)$ is the magnitude (real) of the wave function

and $S(\vec{\mathbf{r}},t)$ is its phase

$$\left[R(\vec{\mathbf{r}},t)\right]^2 = \psi(\vec{\mathbf{r}},t)\psi^*(\vec{\mathbf{r}},t) = \left|\psi(\vec{\mathbf{r}},t)\right|^2$$

$\psi^*(\vec{\mathbf{r}},t)$ is a complex conjugate of $\psi(\vec{\mathbf{r}},t)$

Example

The wave function at a point x on the screen of a particle that passed through the slit labeled 1 in a two-slit apparatus is R(x)exp(iS$_1$(x). The wave function at the same point of a particle that passed through the slit labeled 2 is R(x)exp(iS$_2$(x)).The three functions R(x), S$_1$(x) and S$_2$(x) are real-valued. Show that if both slits are open, the absolute square of the wave function at the screen exhibits an interference pattern.

Solution: With both slits open, the wave function on the screen is:
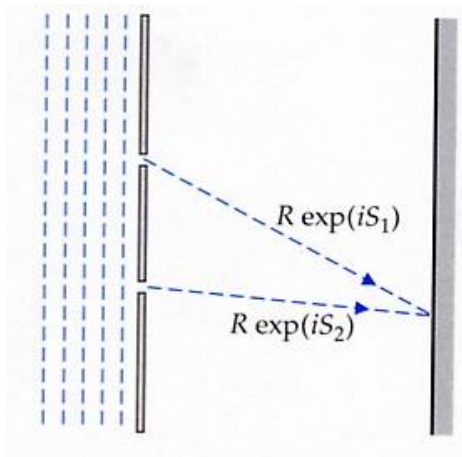
$$\psi(x) = R(x)\exp\big[iS_1(x)\big] + R(x)\exp\big[iS_2(x)\big]$$

Therefore, the square of the absolute value is

$$\big|\psi(x)\big|^2 = \big|R(x)\big|^2 \big[\exp(iS_1) + \exp(iS_2)\big]\big[\exp(-iS_1) + \exp(-iS_2)\big]$$

$$\big|\psi(x)\big|^2 = 2\big|R(x)\big|^2 \big[1 + \cos(S_1 - S_2)\big]$$

As the two phases S$_1$ and S$_2$ vary with position, $\big|\psi(x)\big|^2$ changes between 0 and $4\big|R(x)\big|^2$

This is a standard interference pattern, with regions of destructive and constructive interference.

2.2. Wave function and its probabilistic interpretation

In 1926, German theoretical physicist **Max Born** proposed an interpretation of the wave function $\psi(\vec{r},t)$ that Schrödinger had introduced. His idea was that the square of the absolute value of the wave function measures the probability of finding a particle.

1882-1970

$$\left|\psi(\vec{\mathbf{r}},t)\right|^2 d^3\vec{\mathbf{r}}$$

is proportional to the **probability** of finding an electron at time t in the box of size $d^3\vec{\mathbf{r}}$ around the point $\vec{\mathbf{r}}$

The two-slit experiment reveals itself in an enhanced (constructive interference) or suppressed (destructive interference) *probability* of the arrival of the electrons on the screen

$$\left|\psi(\vec{\mathbf{r}},t)\right|^2 = \left[R(\vec{r},t)\right]^2$$

2.2. Wave function and its probabilistic interpretation

Since, at any given time, the probability of finding an electron somewhere in space is unity, it follows from Born interpretation:

$$\int\limits_{all\ space} \left|\psi(\vec{\mathbf{r}},t)\right|^2 d^3\vec{\mathbf{r}} = 1$$

normalization process

Wave functions used to describe „particles" like electrons are waves of probability. In places where their amplitudes are small, the probability of locating the particle is also small. They have phases, that is why the probability waves can interfere with each other like any kind of a wave.

2.3. The form of Schrödinger equation

Postulates under which the quantum wave equation (Schrödinger equation, SE) was formulated:

1. remain in agreement with de Broglie relation

$$\lambda = \frac{h}{\left|\vec{p}\right|}$$

2. total energy E of the particle is the sum of kinetic and potential energies

$$E = \frac{p^2}{2m} + V(x)$$

3. has to be linear (linear combination of wave functions solves SE if all of them solve it)

2.3. The form of Schrödinger equation

Sound waves and waves on strings are described by equations of Newtonian mechanics. Light waves are described by Maxwell's equations. Matter waves are described by Schrödinger's equation advanced in 1926 by Austrian physicist **Erwin Schrödinger**

1887-1961

$$i\hbar \frac{\partial \psi(\vec{\mathbf{r}},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \psi(\vec{\mathbf{r}},t) + V(\vec{\mathbf{r}})\psi(\vec{\mathbf{r}},t)$$

$$\nabla^2 = \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad \text{Laplacian operator}$$

$V(\vec{\mathbf{r}})$ potential

$\psi(\vec{\mathbf{r}},t)$ wave function

m – mass of the particle

2.3. The form of Schrödinger equation

1887-1961

More often we will be using the **time-dependent** Schrödinger equation in one dimension:

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

It can be written in a form:

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

hamiltonian

Hamiltonian is an operator acting on the wave function. Its eigenvalues represent energy according to the classical formula:

$$E = \frac{p^2}{2m} + V(x)$$

Plane wave as a solution of time-dependent Schrödinger equation

Complex wave function that solves the time-dependent SE in one dimension in the absence of any force V(x)=0 has the following form:

$$\psi(x,t) = A\left[\cos(kx - \omega t) + i\sin(kx - \omega t)\right]$$

This represents the **plane-wave** and can be written as:

$$\psi(x,t) = A\exp\left[i(kx - \omega t)\right]$$

or: $\qquad \psi(x,t) = A\exp\left[\dfrac{i(px - Et)}{\hbar}\right]$ $\qquad \omega = \dfrac{E}{\hbar}$

where: $\quad k = \dfrac{2\pi}{\lambda} = \dfrac{p}{\hbar}$ $\quad$ k is the wave number $\qquad$ ω is the angular frequency

2.4. The time-independent Schrödinger equation

Assuming that potential V(x) is independent of time (stationary conditions) one can solve SE by separation of variables and obtain so-called **time-independent Schrödinger equation**.

This method consists of supposing that the wave function can be written as a product of two functions: *T(t)* dependent on time *t*, only and *u(x)* dependent on position *x*, only:

$$\psi(x,t) = u(x)T(t)$$

Then SE takes a form:

$$i\hbar u(x)\frac{dT(t)}{dt} = T(t)\left(-\frac{\hbar^2}{2m}\frac{d^2}{d^2x}u(x) + V(x)u(x)\right)$$

2.4. The time-independent Schrödinger equation

Dividing by *T(t)u(x),* we get

$$i\hbar \frac{1}{T(t)} \frac{dT(t)}{dt} = \frac{1}{u(x)} \left(-\frac{\hbar^2}{2m} \frac{d^2}{d^2 x} u(x) + V(x)u(x) \right)$$

The two sides of this equation depend on entirely independent variables, the left side on time and the right side on position. The only way to make the equation hold for all time and all positions is for each side to equal a time- and space-independent constant, the same for both sides. We label this constant E and it has the physical meaning (it is the energy of the particle)

2.4. The time-independent Schrödinger equation

We have two equations:

$$i\hbar \frac{dT(t)}{dt} = ET(t)$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{d^2 x}u(x) + V(x)u(x) = Eu(x)$$

The first of these equations isolates the time dependence of the SE and has a direct solution:

$$T(t) = \exp\left(-\frac{iEt}{\hbar}\right)$$

The second of these equations is the so-called **time-independent Schrödinger equation**. We have to solve it for each particular potential V(x).

2.4. The time-independent Schrödinger equation

The solution to time-dependent Schrödiger equation is :

$$\psi(x,t) = u_E(x) \exp\left(-\frac{iEt}{\hbar}\right)$$

We may write:

$$\hat{H} u_E(x) = E u_E(x)$$

Hamiltionian operator $\hat{H}$

$u_E(x)$ is an eigenfunction of the Hamiltonian operator, E is the corresponding eigenvalue of that operator

The problem of solving the SE comes down to finding eigenfunctions and eigenvalues of the HAMILTONIAN

Large potential at the edges of the infinite well acts to prevent the escape of electrons. The motion of an electron is restricted to the region 0<x<L; in that region the electron is free.

V(x) infinity   V(x)=0   V(x) infinity   u(x)=0 outside the well, probability density vanishes outside the well

In the region inside the well, i.e. for 0<x<L, the time-independent SE is:

x=0   x=L
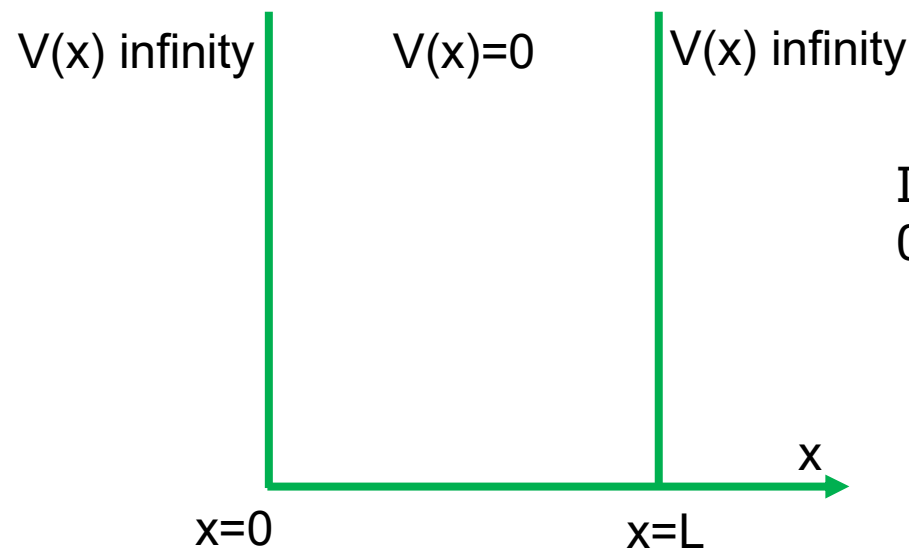
The potential is zero inside the box, and infinity outside

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}u(x) = Eu(x)$$

Boundary conditions:

$$u(0) = u(L) = 0$$

2.5. Example of solution of SE – the infinite well

Proposed solution is:

$$u_E(x) = A\sin(kx)$$

where A is a constant that we can eventually use for normalization

discrete energy levels

Proposed function satisfies SE provided that:

$$E = \frac{\hbar^2 k^2}{2m}$$

We apply the boundary conditions: for x=L, u_E=0

This means: $\sin(kL) = 0$ $\Longrightarrow$ $kL = n\pi$ with n=1,2,…

In other words, *E takes on only discrete values*

Energy is quantized

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2$$

$25E_0$ ————— $n = 5$

$16E_0$ ————— $n = 4$

$9E_0$ ————— $n = 3$

$4E_0$ ————— $n = 2$

E_0 ————— $n = 1$
$E = 0$
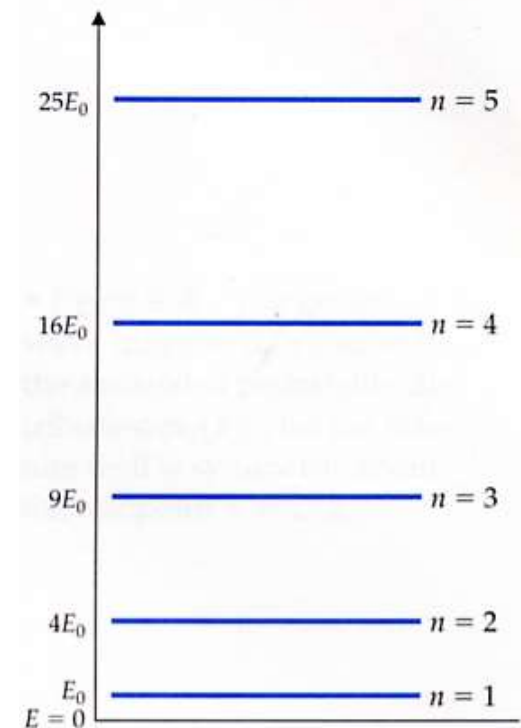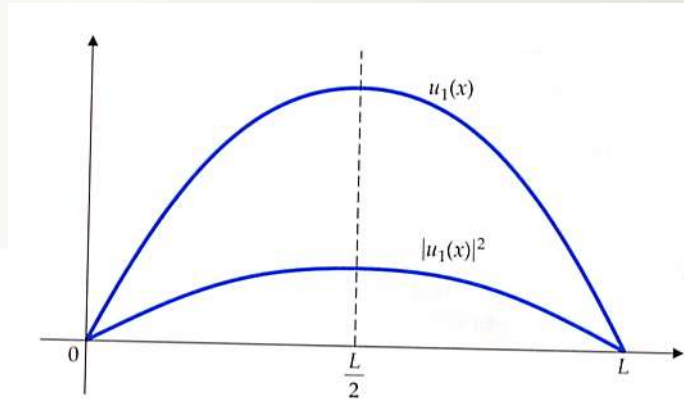
The solutions

$$u_n(x) = A \sin(\frac{n\pi}{L} x)$$

correspond to standing waves with a different number n of nodes within the potential well
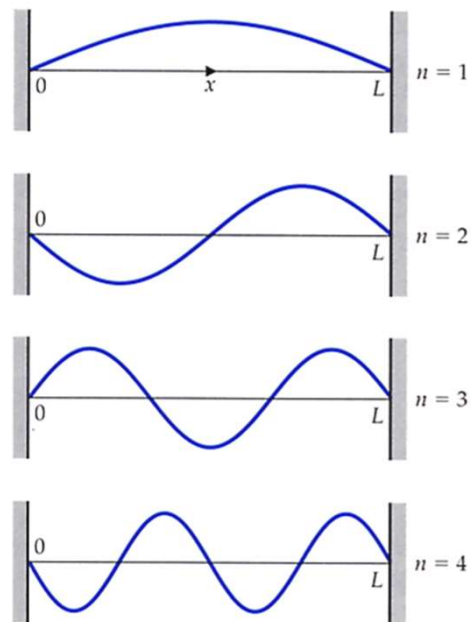
Eigenfunctions $u_n(x)$ for the infinite well
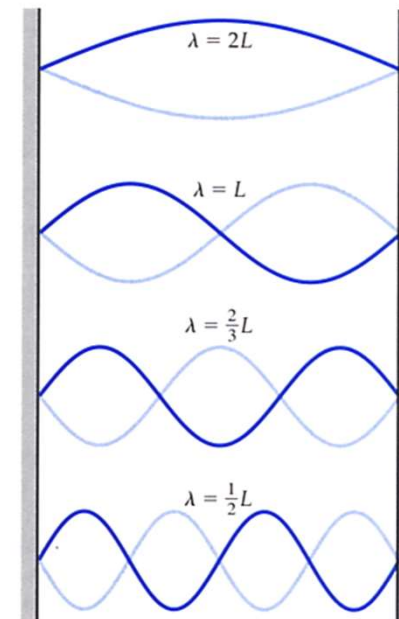
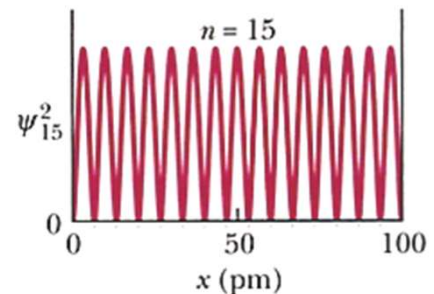Allowed modes of oscillation of a classical string with its ends fixed
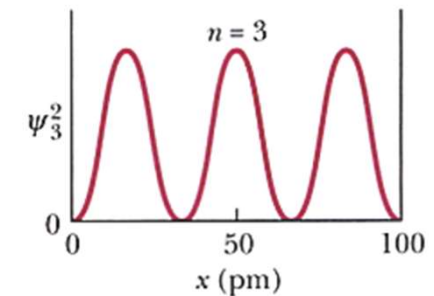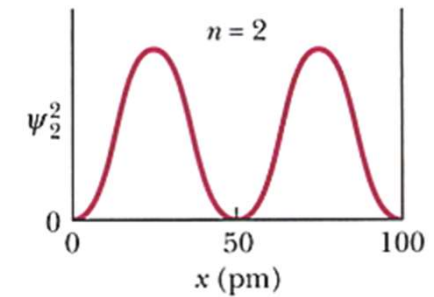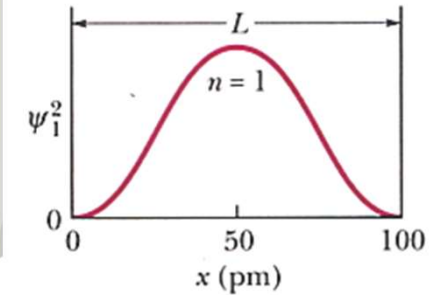
The ground-state wave function $u_1(x)$ as well as the associated probability distribution $|u_1(x)|^2$

Properly normalized ground-state wave function is:

$$u_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

the subscript is the value of n

Probability distribution for ground (n=1) and excited states (n>1)

2.6. The physical meaning of eigenfunctions and eigenvalues

When a wave function satisfies the Schrödinger equation, it is an eigenfunction of the Hamiltonian operator with eigenvalue given by energy of particle, *E.* Such waves represent particles with definite energy.

It is generally true that, for an eigenfuction of an operator representing some physical variable, a measurement of that variable will always yield the eigenvalue.

It follows that the momentum operator is:

$$\hat{p}_x = -i\hbar \frac{\partial}{dx} \qquad \hat{p}_y = -i\hbar \frac{\partial}{dy} \qquad \hat{p}_z = -i\hbar \frac{\partial}{dz}$$

Its eigenvalues represent the measured value of the momentum *p*

$$-i\hbar \frac{d}{dx} u_p(x) = p u_p(x)$$

Conclusions

- The Schrödinger equation, SE is the counterpart of classic equations for waves (electromagnetic, sound, etc.) It is a partial differential equation involving second-order spatial derivatives and first-order temporal derivatives.

- The wave function of a particle under the influence of various forces satisfies the Schrödinger equation. The wave function is a complex-valued function of space and time. Its physical significance is that the square of the absolute value of the function describes the probability that the particle is at a given location in space at a given time.

- Knowledge of the wave function allows to find the probabilities that the particle has certain values of momentum, energy, or other physically measurable quantities.

- The time dependence of the SE can often be factored out of the equation leaving the so-called time-independent Schrödinger equation, which determines the allowed values of energy, or energy eigenvalues. In situations in which the particle is bound or confined, these energies are restricted to certain discrete, or quantized, values. For each allowed energy, there is specific time-independent function, forming a set of energy eigenfunctions.