Unit – 3: Quantum Theory

Quantum Theory : Planck’s radiation formula, Ultraviolet catastrophe, Compton’s effect, de Broglie’s concept of matter waves, Heisenberg’s uncertainty relations, Schrodinger’s wave equation, Physical interpretation of wave function, Particle in a one-dimensional potential well.

Planck’s radiation Formula & Ultraviolet Catastrophe

Blackbody Radiation

At the end of 19th Century scientists believed that the laws of Physics (which were known at that time) are enough to explain all the events Occur in nature. It was felt that there are two kinds, one is particles which obey Newton’s laws of motion & Second is radiations, obey Maxwell's equations of electromagnetism. These laws at that time is known as Classical Physics.

But few experiments like Blackbody Radiation, Photoelectric effect, Compton's effect etc, the experiments in which there was interaction between radiation a matter were not explained by Classical physics. In order to explain these effects new mechanics was required, called as Quantum mechanics. So blackbody radiation is one of the great effects that leads to modern physics.

Blackbody

Radiation that is incident on an object is partially absorbed and partially reflected. At thermodynamic equilibrium, the rate at which an object absorbs radiation is the same as the rate at which it emits it. *Therefore, a good absorber of radiation (any object that absorbs radiation) is also a good emitter*. A perfect absorber absorbs all electromagnetic radiation incident on it; such an object is called a **blackbody**.

Blackbody Radiation

Although the blackbody is an idealization, because no physical object absorbs 100% of incident radiation, we can construct a close realization of a blackbody in the form of a small hole in the wall of a sealed enclosure known as a cavity radiator, as shown in Figure 1. The inside walls of a cavity radiator are rough and blackened so that any radiation that enters through a tiny hole in the cavity wall becomes trapped inside the cavity. At thermodynamic equilibrium (at temperature T), the cavity walls absorb exactly as much radiation as they emit. Furthermore, inside the cavity, the radiation entering the hole is balanced by the radiation leaving it. The emission spectrum of a blackbody can be obtained by analyzing the light radiating from the hole. Electromagnetic waves emitted by a blackbody are called blackbody radiation.

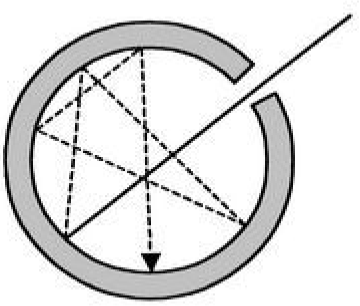


Figure 1. A schematic of a blackbody. At thermal equilibrium all radiation absorbed and also emitted.

The Temperature & the body is kept fixed & this implies that the radiation is in thermal equilibrium, which mean the electromagnetic radiations emitted per second by the walls of Cavity is Same as the radiations absorbed. The energy density of the electromagnetic radiation remains Constant, as the system is in thermal equilibrium. Also, there's a hole in the Cavity which allows the radiation to Come out.

Energy Density:

At a Particular temperature T energy in the Cavity per unit volume is called energy density. It is denoted by u.

Spectral Energy Density

At a certain temperature the average energy density between wavelength λ and λ + d λ is given by u_λ d λ where u_λ is called spectral energy density. The relation between u and u_λ is given by

$$U = \int_0^\infty u_\lambda d\lambda \tag{1}$$

one can use u_υ, instead of u_λ, which is defined frequency range between υ and υ+dυ .

Emissive Power

Total radiation energy emitted by unit surface area of the blackbody at a certain temperature is called Emissive Power of the blackbody.

Spectral Emissive power

Total radiated energy between λ and λ + d λ wavelength range emitted by unit surface area of blackbody at Certain temperature is given by E_λd λ where E_λ is called spectral emissive power of black body. It is clear from the definition that

$$E = \int_0^\infty E_\lambda \, d\lambda \tag{2}$$

If we know E_λ at certain temperature, then u_λ can be found a

$$U = \frac{4}{c} E_\lambda \tag{3}$$

Where c is speed of light.

Experimental study of Blackbody Radiation

First attempt was made by Lummer & Pringsheim in 1899. They plotted some curves between E_λ and λ for various temperatures as shown below in fig. (1). These plots are known as spectral energy distribution curve of blackbody radiation.

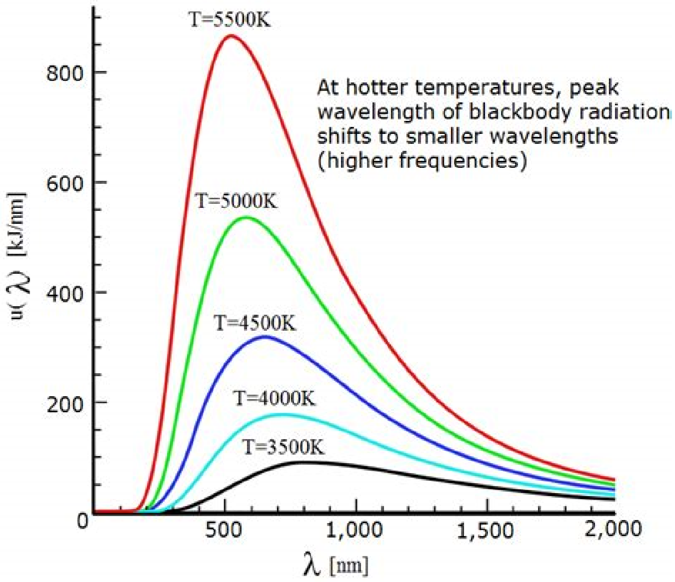


Figure 2:.The spectrum of black-body radiation with increasing temperature showing blue shift at high temperatures.

Characteristics of Blackbody radiation.

1. It is clear from the figure that the graph is continuous which means, at every temperature, radiation for all wavelengths emitted the spectral emissive power is different for different wavelengths.
2. Spectral energy density E_λ for each λ increases with temperature.
3. At a Particular temperature at first E_λ increases with λ but after reaching certain highest value it goes decreasing. The highest value is cloned by $E_{\lambda m}$ & wavelength at which E_λ is maximum is denoted by λ_m.
4. Wien's Displacement Law – As we see from the graph λ_m decreases with temperature, It was Wien who first mathematically discovered

$$\lambda_m \propto \frac{1}{T}$$

or $$\lambda_m = \frac{b}{T} \tag{4}$$

where b is Wien's Constant value is b= 2.898 x10^{-3} meter-kelvin. The above law is known as Wien's displacement law. It Can be also expressed in terms of frequency as

$$U_m = \frac{cT}{b} \qquad (5)$$

We also see that the peak of the graph Increases rapidly with temperature. It is found that

$$E_{\lambda m} \propto T^{-5} \qquad (6)$$

5. Stephan's Boltzmann's Law- At a particular temperature the area under the curve is given by $\int_0^\infty E_\lambda \mathrm{d}\,\lambda$, which is the is total emissive Power of blackbody. Hence the area of the curve represents total emissive power. It is found to be proportional to T^4 i.e.

$$E = \sigma T^4 \qquad (7)$$

where σ = Stephan's constant having value σ = $5.67\text{x}10^{-8}$ watt/m^2/K^4. This law is known Stefan Boltzmann's law. Many attempts were made to explain the blackbody radiation curve. Wien's and Rayleigh Jeans distribution law were used to explain the spectral distribution of blackbody radiations, but neither of these laws were able to explain it completely.

Wien's Distribution Law

Wien used thermodynamics to show that the Spectral density between λ and λ + d λ wavelength range is given by

$$E\lambda\, d\lambda = \frac{A}{\lambda^5} f(\lambda T)\, d\lambda \qquad (8)$$

To find the form of function $f(\lambda T)$, he compared blackbody distribution curve with Maxwellian energy distribution curve. After the Comparison he deduced

$$f(\lambda T) = e^{-a/\lambda T}$$

hence, he found

$$E\lambda\, d\lambda = \frac{A}{\lambda^5} e^{-a/\lambda T}\, d\lambda \qquad (9)$$

Where A and a are constants, T is temperature in Kelvin. This equation (9) is known as Wien's distribution law. Wien's law works well only for shorter wavelengths. There are considerable deviations at longer wavelengths & high temperature. In equation 9, when temperature is infinite (T=∞), the energy density $E\lambda$ is finite. This is in contradiction to experimentally verified Stefan's law. This implies an error in the theoretical distribution law & indicates flaws in the theory. Wien Could neither explained the failure his relation nor supply a better one.

Rayleigh Jeans Distribution Law

In 1900 Rayleigh & Jeans used Maxwell Boltzmann statistics to derive anther distribution in order to explain blackbody radiation. According to Rayleigh, the radiation waves in blackbody can be compared to the standing waves in the cubical cavity and hence he calculated number of modes in wavelength range λ and $\lambda + d\lambda$

$$N\lambda \, d\lambda = \frac{8\pi}{\lambda^4} \tag{10}$$

As Per the principle of equipartition of energy. assignment of an average energy of kT to each mode of vibration leads to an energy density $U\lambda \, d\lambda$ for waves with wavelength range λ and $\lambda + d\lambda$ given by

$$U\lambda \, d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda \tag{11}$$

Above equation is known as Rayleigh Jeans formula blackbody radiation. It contains no new Constants. In Rayleigh Jeans formula the energy density $U\lambda$ in a given wavelength range $d\lambda$ increases rapidly as λ decreases and approaches infinity for very short wavelengths, which is not true. Later on Paschen showed that Wien's formula agreed with the experimental curves for shorter wavelengths while Rayleigh formula agreed with longer wavelengths. As none these formulae could account the entire radiation curve, Paschen Suggested that the fundamental assumptions of classical theory were at fault.

The Ultraviolet Catastrophe

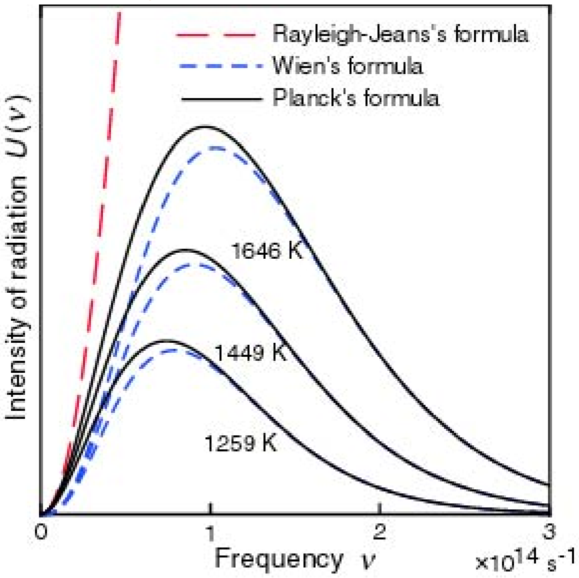


Figure 3 Classical thermodynamic principles Rayleigh-Jeans' formula and Wien's displacement law could not explain Blackbody ration at high temperatures called UV catastrophe. While Planck's theory provides perfect matching.

From equation (11) we see that energy density decreases with λ, which is correct only in the higher wavelength region. Hence Rayleigh Jeans distribution law holds only for larger λ part. At small λ this law Rayleigh Jeans law fails. The most disturbing aspect of Rayleigh Jeans law is that the area under the curve is infinite, this area represents the total energy radiated by the black body. The Rayleigh Jeans law forecasts that a body at temperature let 500K will radiate energy at an infinite rate!

There is nothing about 500K the law predicts infinite total radiation for all blackbodies, even those with temperature 0.01K. This nonsensical result became known as the “ULTRAVIOLET CATASTROPHE” because the excess radiation is found at short wavelength in UV region. It signalled a fundamental flaw in Classical thermodynamics.

As was the case with Wien distribution law. So, Wien as well as Rayleigh Jeans couldn’t improve the prediction.

Failure of Classical Physics

Thus, we have two theoretical relations equation (9) and (11) Produced by Wien and Rayleigh Jeans to explain the black body radiation. The First equation is good at shorter wavelength but inadequate at longer, while the second one is poor in IR and ridiculous in UV. Thus, both the physicists could not produce Satisfactory explanation of blackbody radiation through classical thermodynamics.

Need of new mechanics

As the Classical Physics or the Classical laws were unable to solve the Blackbody Radiation curve completely, so in order to explain the interaction of radiation with matter a new mechanics was needed. In this Max Planck gave a new and brave idea to solve this Blackbody radiation puzzle through quantum mechanics, which is called as Quantum hypothesis or Planck’s quantum hypothesis. Plank in 1901 proposed a new revolutionary hypothesis also called as theory of quanta or photons.

Planck's Hypothesis

In order to explain the experimentally observed distribution of energy in the spectrum of blackbody, Planck suggested that the correct results can be obtained if the energy of oscillating electrons is taken discreet rather than continuous. He derived the radiation law using assumptions which are:

(i) A cavity containing blackbody radiations also contains Simple harmonic oscillators of molecular dimensions which can Liberate with all possible frequencies.

(ii) The frequency of radiation emitted by an oscillator is same as the frequency of its vibration.

(iii) An oscillator cannot emit energy in continuous manner, it can emit energy in the multiples of small unit called as quantum (photon). If an oscillator is vibrating with frequency υ, it can only radiate in quanta of magnitude hυ, i.e. oscillator can have only discreet energy values

$$E_n = nh\nu \qquad (12)$$

Where n is an integer and h is Planck’s constant whose value is 6.62 x 10^{-34} Js.

(iv) The Oscillators can emit or absorb radiation energy in packets of hυ. This assumption is most revolutionary in character. It implies that the exchange energy between radiation and matter cannot take place continuously but are limited to discrete set of values like

$0, h\upsilon, 2h\upsilon, 3h\upsilon, 4h\upsilon,\ldots\ldots\ldots\ldots\ldots n h\upsilon.$

Planck's Radiation law

Average energy of Planck Oscillator

Planck used Maxwell Boltzmann Statistics to calculate radiation energy. According to Planck at temperature T, the number of oscillators having energy $nh\upsilon$ is

$$N_n = A\exp\left(\frac{-nh\upsilon}{kT}\right) \qquad \text{-(13)}$$

where k is Boltzmann Constant, h is Planck's Constant. The total energy of oscillator having energy n hυ is

$$E_n = n\,h\upsilon\,N_n \qquad \text{-(14)}$$

Hence the total energy of all oscillators in blackbody

$$E_n = \Sigma\, E_n = \Sigma\, nh\upsilon\, N_n \qquad \text{-(15)}$$

Total number of oscillations in the blackbody is

$$N = \Sigma\, N_n$$

⟹ Average energy of Oscillator is

$$< E > = \frac{Total\ energy\ of\ oscillator}{Total\ number\ of\ Oscillator} \qquad \text{-(16)}$$

$$< E > = \frac{\Sigma\, nh\upsilon\, Nn}{\Sigma\, Nn}$$

$$= \frac{\Sigma\, nh\upsilon \exp(-nh\upsilon/kT)}{\Sigma \exp(-nh\upsilon/kT)} \qquad \text{-(17)}$$

Let x = hυ/KT

⟹

$$< E > = \frac{KT\,\Sigma\, nx\exp(-nx)}{\Sigma \exp(-nx)} \qquad \text{-(18)}$$

$$= \ < E > = -x\,kT\,\frac{d/dx[\Sigma \exp(-nx)\,]}{\Sigma \exp(-nx)}$$

But $$\Sigma\ \exp(-nx) = \frac{1}{1-e^{-x}}$$

And $$d/dx[\Sigma \exp(-nx)] = \frac{-e^{-x}}{(1-e^{-x})2}$$

Therefore $$< E > = \frac{\frac{-e^{-x}}{(1-e^{-x})2}}{\frac{1}{1-e^{-x}}}$$

⟹

$$< E > = \frac{x\,kT}{(e^{-x}-1)} \qquad \text{- (19)}$$

Hence average energy of an oscillator is

$$< E > = \frac{h\nu}{(e^{\frac{h\upsilon}{kT}}-1)} \qquad - (20)$$

In terms of wavelength

$$< E > = \frac{hc/\lambda}{(e^{\frac{hc}{\lambda kT}}-1)} \qquad - (21)$$

Complete Distribution Law

According to Planck energy density between range is λ and λ + d λ is

$$U\lambda\, d\lambda = N\lambda d\lambda <E>$$

Planck used the calculation made by Rayleigh Jeans for number of Oscillations. Hence

$$N\lambda\, d\lambda = \frac{8\pi}{\lambda^4}\, d\lambda$$

Thus, in terms of wavelength

$$U\lambda\, d\lambda = \frac{8\pi hc}{\lambda^5\,(e^{\frac{hc}{\lambda kT}}-1)}\, d\lambda \qquad - (22)$$

In terms of frequency $$U\upsilon\, d\upsilon = \frac{8\pi h\nu^3}{c^3\ \exp(\frac{h\nu}{KT})-1}\quad d\upsilon \qquad - (23)$$

The above equation is called as Planck's distribution law.

Having Postulated quantization and derived a fine radiation law (it fitted the data spectacularly well and avoided UV catastrophe), it explained the problem of blackbody radiation with remarkable accuracy of wavelength. For Small wavelength it reduces to Wien's distribution law while in larger wavelength range it is similar to Rayleigh Jeans law.

Explanation in small $\boldsymbol{\lambda}$ range or Wien’s law

For hc/kT » 1

$\exp\,(\frac{hc}{kT})$ » 1, here 1 can be neglected, so using this in Planck’s law

$$U\lambda\, d\lambda = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{e^{(\frac{hc}{\lambda kT})}}\right] d\lambda$$

$$\Rightarrow \quad U\lambda\, d\lambda = \frac{8\pi hc}{\lambda^5}\exp(-\frac{hc}{\lambda kT})\, d\lambda \qquad - (24)$$

This equation is similar to Wien's distribution law which is correct for small wavelengths. Hence from Planck’s Radiation Law Wien's distribution law can be derived.

Explanation in long wavelength region or Rayleigh Jean’s Law

If hc/kT « $\boldsymbol{\lambda}$

then, exp (hc/kT) = 1+ (hc/kT). Using this in Planck's law we get

$$U\lambda\, d\lambda = \frac{8\pi hc}{\lambda^5}\,\frac{1}{\frac{hc}{\lambda kT}}$$

i.e.

$$U\lambda\, d\lambda = \frac{8\pi kT}{\lambda^4}\, d\lambda \qquad - (25)$$

which is Rayleigh Jeans distribution law. It can explain all the properties of blackbody radiation at large wavelengths.

1. Classical physics could not explain the behavior of a black body radiation at very short wavelengths. What was this problem called?
   (A) Ultraviolet Catastrophe (B) Absorption failure
   (C) Wavelength decrease (D) Photoelectric Effect
   (E) Radiation

2. What did Max Planck propose to solve the black body radiation problem?
   (A). Light comes in packets of energy. (B) Light changes its speed in different media.
   (C). Radiation is made up of waves (D) Light has a continuous energy profile.
   (E) Objects do not radiate energy.

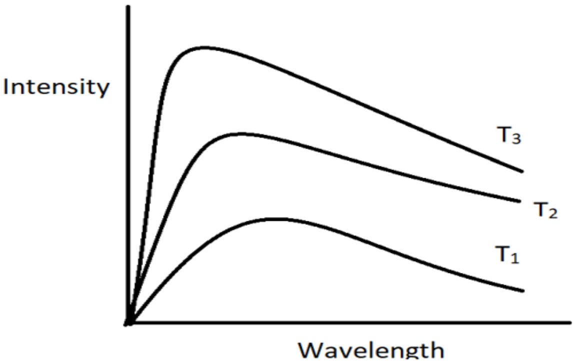
3. The energy of a photon depends on its:
   (A) Frequency (B) Speed (C) Temperature (D) Pressure (E) Amplitude

4. How does the energy of a photon change if the wavelength is doubled?
   (A) Is cut to one-half (B) Quadruples (C) Stays the same
   (D) Doubles (E) Is cut to one-fourth

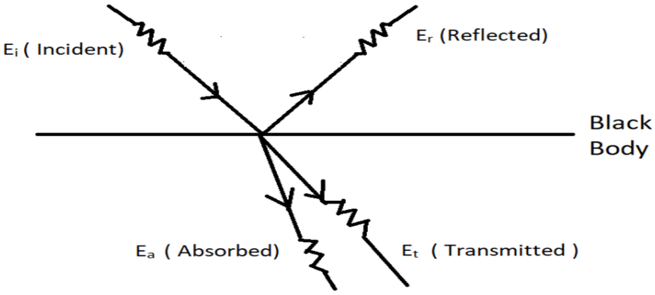
5. As the wavelength of the radiation decreases, the intensity of the black body radiations
   a) Increases
   b) Decreases
   c) First increases then decrease
   d) First decreases then increase
6. The radiations emitted by hot bodies are called as ________________
   a) X-rays
   b) Black-body radiation
   c) Gamma radiations
   d) Visible light
7. An iron rod is heated. The colors at different temperatures are noted. Which of the following colors shows that the iron rod is at the lowest temperature?

a) Red
b) Orange
c) White
d) Blue

8. A black body is defined as a perfect absorber of radiations. It may or may not be a perfect emitter of radiations.
   a) True
   b) False
9. From the figure, what's the relation between T_1, T_2, and T_3?



   a) $T_1 > T_2 > T_3$
   b) $T_3 > T_2 > T_1$
   c) $T_3 > T_1 > T_2$
   d) $T_2 > T_1 > T_3$
10. Electromagnetic wave theory of light could not explain Black Body radiations.
    a) True
    b) False
11. What is the relation between the Energies as shown in the figure?



    a) $E_r = 0$
    b) $E_a = 0$
    c) $E_t = E_i$
    d) $E_i = E_r$

COMPTON EFFECT

According to the quantum theory of light, photons behave like particles except for their lack of rest mass. How far can this analogy be carried? For instance, can we consider a collision between a photon and an electron as if both were billiard balls.

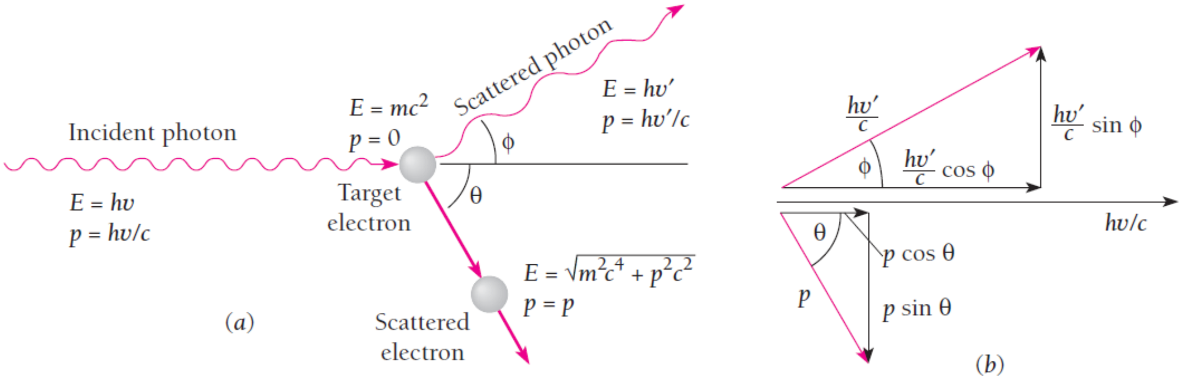


Figure 4: (a) The scattering of a photon by an electron is called the Compton effect. Energy and momentum are conserved in such an event, and as a result the scattered photon has less energy (longer wavelength) than the incident photon. (b) Vector diagram of the momenta and their components of the incident and scattered photons and the scattered electron.

Figure 5, shows such a collision: an x-ray photon strikes an electron and is scattered away from its original direction of motion while the electron receives an impulse and begins to move. We can think of the photon as losing an amount of energy in the collision that is the same as the kinetic energy KE gained by the electron, although actually separate photons are involved. If the initial photon has the frequency ν associated with it, the scattered photon has the lower frequency ν'. From the principle of conservation of energy, we may write

Theory of Compton Effect

Loss in photon energy = gain in electron energy

$$h\nu - h\nu' = K.E. \tag{1}$$

The momentum of a massless particle is related to its energy by the formula

$$E = pc \tag{2}$$

Since the energy of a photon is $h\nu$, its momentum is

$$p = \frac{E}{c} = \frac{h\nu}{c} \tag{3}$$

Momentum, unlike energy, is a vector quantity that incorporates direction as well as magnitude, and in the collision momentum must be conserved in each of two mutually perpendicular directions. The directions we choose here are that of the original photon and one perpendicular to it in the plane containing the electron and the scattered photon.

The initial photon momentum is $h\nu/c$, the scattered photon momentum is $h\nu'/c$, and the initial and final electron momenta are respectively 0 and p. In the original photon direction (see Figure 5(b))

Initial momentum = final momentum

$$\frac{h\nu}{c} + 0 = \frac{h\nu'}{c} \cos\varphi + p\cos\theta \qquad (4)$$

and perpendicular to this direction

Initial momentum = final momentum

$$0 + 0 = \frac{h\nu'}{c} \sin\varphi + p\sin\theta \qquad (5)$$

The angle φ is that between the directions of the initial and scattered photons, and θ is that between the directions of the initial photon and the recoil electron. From Eqs.(1) – (5), we can find a formula that relates the wavelength difference between initial and scattered photons with the angle φ between their directions, both of which are readily measurable quantities (unlike the energy and momentum of the recoil electron).

he first step is to multiply Eqs. (4) and (5) by c and rewrite them as

$$pc\cos\theta = h\nu - h\nu'\cos\varphi$$

$$pc\sin\theta = h\nu'\sin\varphi$$

By squaring each of these equations and adding the new ones together, the angle θ is eliminated, leaving

$$p^2c^2 = (h\nu)^2 - 2(h\nu)(h\nu')cos\varphi(h\nu)(h\nu')\cos\varphi + (h\nu')^2 \qquad (6)$$

Next we equate the two expressions for the total energy of a particle

$$E = K.E. + mc^2 \qquad (7)$$

and

$$E = \sqrt{m^2c^4 + p^2c^2} \qquad (8)$$

Hence

$$(K.E. + mc^2)^2 = m^2c^4 + p^2c^2$$

$$p^2c^2 = K.E.^2 + 2mc^2 K.E.$$

Since, $K.E. = h\nu - h\nu'$, we have

$$p^2c^2 = (h\nu)^2 - 2(h\nu)(h\nu') + (h\nu')^2 - 2mc^2(h\nu - h\nu') \qquad (9)$$

Substituting this value of p^2c^2 in Eq. (8), we finally obtain

$$2mc^2(h\nu - h\nu') = 2(h\nu)(h\nu')(1 - \cos\varphi) \qquad (10)$$

Dividing the above equation (10) by $2h^2c^2$, we obtain

$$\frac{mc}{h}\left(\frac{\nu}{c} - \frac{\nu'}{c}\right) = \frac{\nu}{c}\frac{\nu'}{c}(1 - cos\varphi)$$

$$\frac{mc}{h}\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right) = \frac{1}{\lambda}\frac{1}{\lambda'}(1 - cos\varphi)$$

Or it can be simplified as

$$\lambda' - \lambda = \lambda_c(1 - cos\varphi) \qquad (11)$$

With $\lambda_c = h/mc$ (= 2.426 pm), is called Compton wavelength.

The Compton wavelength gives the scale of the wavelength change of the incident photon. From Eq. (11) we note that the greatest wavelength change possible corresponds to $\varphi = 180°$, when the wavelength change will be twice the Compton wave-length λ_C. Because λ_C =2.426 pm for an electron, and even less for other particles owing to their larger rest masses, the maximum wavelength change in the Compton effect is 4.852 pm. Changes of this magnitude or less are readily observable only in X-rays: the shift in wavelength for visible light is less than 0.01 percent of the initial wavelength, whereas for X-rays of λ = 0.1 nm it is several percent. The Compton effect is the chief means by which X-rays lose energy when they pass through matter.

Experimental Results

The experimental demonstration of the Compton effect is straightforward. As in Figure 6, a beam of X-rays of a single, known wavelength is directed at a target, and the wavelengths of the scattered X-rays are determined at various angles φ. The results, shown in Figure 7, exhibit the wavelength shift predicted by Eq. (11), but at each angle the scattered X-rays also include many that have the initial wavelength. This is not hard to understand. In deriving Eq. (11) it was assumed that the scattering particle is able to move freely, which is reasonable since many of the electrons in matter are only loosely bound to their parent atoms. Other electrons, however, are very tightly bound and when struck by a photon, the entire atom recoils instead of the single electron.

In this event the value of m to use in Eq. (11) is that of the entire atom, which is tens of thousands of times greater than that of an electron, and the resulting Compton shift is accordingly so small as to be undetectable.

Significance

The Compton effect is first successful confirmation for the particle nature of electromagnetic radiation. The em radiation when assumed as a quantum particle or photon, the results exactly matches with the theoretical expression given in eq (11). While this experiment could not be assumed using classical wave theory. Where a wave does not have a momentum and does not interact with a particle like electrons. Hence, this experiment and its results provide a kick-start to field of quantum mechanics.

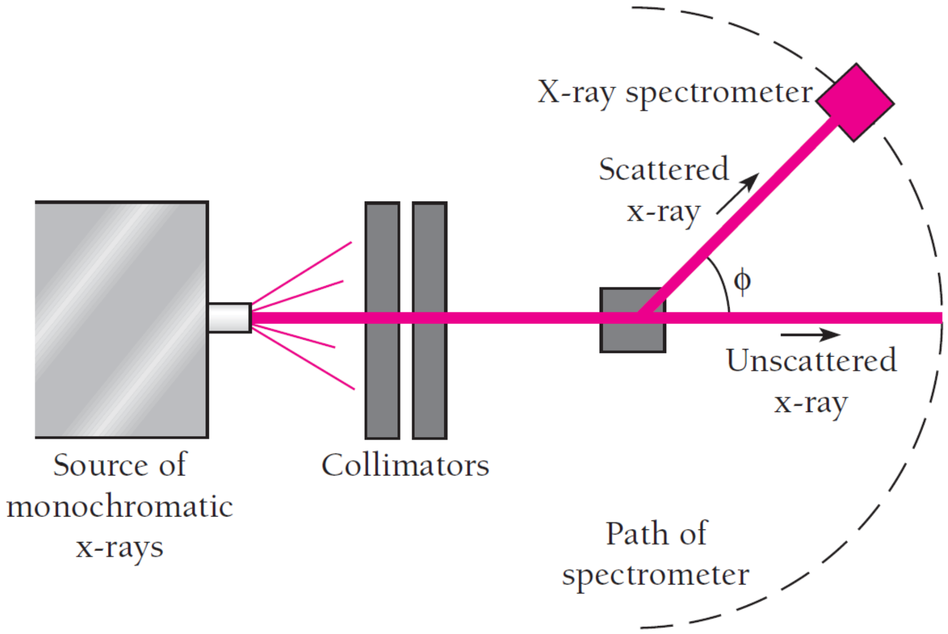


Figure 5: A diagram of Experimental setup for Compton Effect

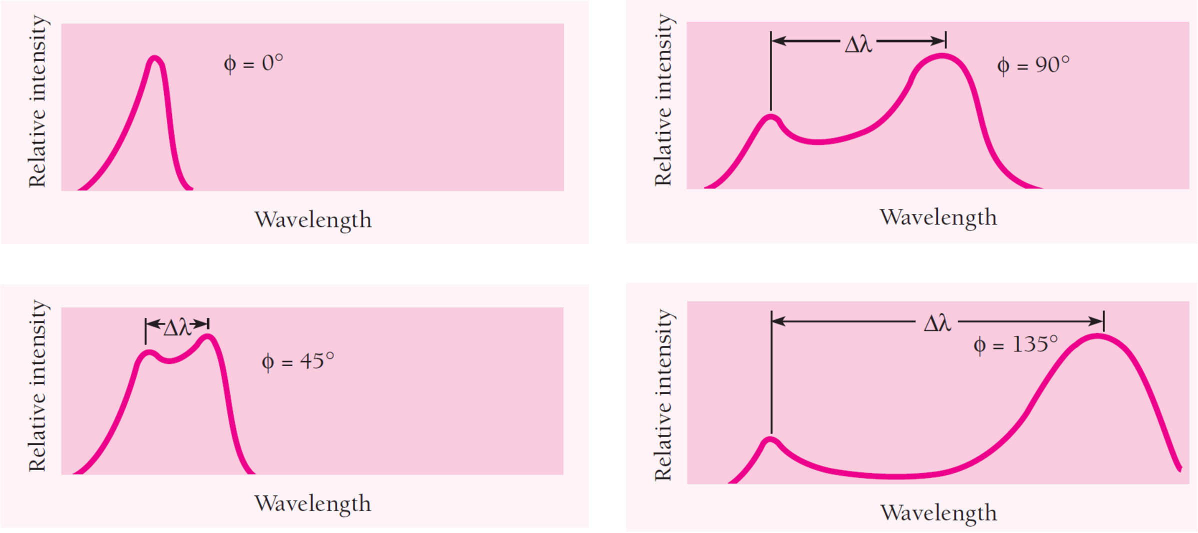


Figure 6: Experimental confirmation of Compton scattering. The greater the scattering angle, the greater the wavelength in accordance with eq. (11)

Solve the following:

1. What is the frequency of an x-ray photon whose momentum is 1.1×10^{-23} kg m/s?
2. How much energy must a photon have if it is to have the momentum of a 10-MeV proton?

3. A monochromatic x-ray beam whose wavelength is 55.8 pm is scattered through 46°. Find the wavelength of the scattered beam.
4. A beam of x-rays is scattered by a target. At 45° from the beam direction the scattered x-rays have a wavelength of 2.2 pm. What is the wavelength of the x-rays in the direct beam?
5. An x-ray photon whose initial frequency was 1.5 x 10^{19} Hz emerges from a collision with an electron with a frequency of 1.2 x 10^{19}, Hz. How much kinetic energy was imparted to the electron?
6. An x-ray photon of initial frequency 3.0 x 10^{19} Hz collides with an electron and is scattered through 90°. Find its new frequency.
7. Find the energy of an x-ray photon which can impart a maximum energy of 50 keV to an electron.
8. At what scattering angle will incident 100-keV x-rays leave a target with an energy of 90 keV?
9. (*a*) Find the change in wavelength of 80-pm x-rays that are scattered 120° by a target. (*b*) Find the angle between the directions of the recoil electron and the incident photon. (*c*) Find the energy of the recoil electron.
10. A photon of frequency ν is scattered by an electron initially at rest. Verify that the maximum kinetic energy of the recoil electron is $KE_{max} = \frac{2h^2\nu^2}{mc^2}\left(1 + \frac{2h\nu}{mc^2}\right)$.
11. In a Compton-effect experiment in which the incident x-rays have a wavelength of 10.0 pm, the scattered x-rays at a certain angle have a wavelength of 10.5 pm. Find the momentum (magnitude and direction) of the corresponding recoil electrons.
12. A photon whose energy equals the rest energy of the electron undergoes a Compton collision with an electron. If the electron moves off at an angle of 40° with the original photon direction, what is the energy of the scattered photon?
13. A photon of energy *E* is scattered by a particle of rest energy E_0. Find the maximum kinetic energy of the recoiling particle in terms of *E* and E_0.

De Broglie Hypothesis

de Broglie equation states that a matter can act as waves much like light and radiation which also behave as waves and particles (Plank's quantum theory). The equation further explains that a beam of electrons can also be diffracted just like a beam of light. The hypothesis helps us to understand the idea of matte having a wavelength and sys that, if we look at every moving particle whether it is microscopic or macroscopic it will have a wavelength. In cases of macroscopic objects, the wave nature of matter can be detected or it is visible.

The de Broglie equation is basically describes the wave nature of the electron. An electromagnetic radiation, exhibit dual nature of a particle (having a momentum) and wave (expressed in frequency, wavelength). Microscopic particle-like electrons also proved to possess this dual nature property. Louis de Broglie in his PhD thesis suggested that any moving particle, whether microscopic or macroscopic will be associated with a wave character. It was called 'Matter Waves'. He further proposed a relation between the velocity and momentum of a particle with the wavelength if the particle had to behave as a wave. ***Particle and wave nature of matter, however, looked contradictory as it was not possible to prove the existence of both properties in any single experiment. This is because of the fact that every experiment is normally based on some principle and results related to the principle are only reflected in that experiment and not the other. Nonetheless, both the properties are necessary to understand or describe the matter completely. Hence, particles and wave nature of matter are actually 'complimentary' to each other. It is not necessary for both to be present at the same time though.*** The significance of de Broglie relation is that it is more useful to microscopic, fundamental particles like electron. **Dual behavior of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other types of material.**

Derivation of expression for de Broglie Wavelength

Very low mass particles moving at speed less than that of light behaves like a particle and wave. De Broglie derived an expression relating the mass of such smaller particles and its wavelength.

Plank's quantum theory relates the energy of an electromagnetic wave to its wavelength (λ) or frequency (ν) such as $E = h\nu = hc/\lambda$, here 'h' is the Plank's constant. Einstein related the energy of particle matter to its mass and velocity, as $E = mc^2$

As the smaller particle exhibits dual nature, and energy being the same, de Broglie equated both these relations for the particle moving with velocity 'v' as,

$$E = \frac{hv}{\lambda} = mv^2 \quad \text{Then,} \quad \frac{h}{\lambda} = mv = \text{momentum } (p), \quad \lambda = \frac{h}{p}$$

This equation relating the momentum of a particle with its wavelength is de Broglie equation and the wavelength calculated using this relation is de Broglie wavelength.

de Broglie Equation and Bohr's Hypothesis of Atom

Bohr postulated that angular momentum of an electron revolving around the nucleus as quantized. Hence, the angular momentum will only be an integral multiple of a constant value and suggested the following expression. Angular momentum of electron in orbit (mvr) is

$$\mathrm{mvr} = \frac{\mathrm{nh}}{2\pi}, \qquad \text{here } \mathrm{n} = 1,2,3 \ldots\ldots$$

Bohr did not give any reason for such a proposal. But, de Broglie equation gives a scientific validation for such an imaginative proposal. The electron wave in an orbit must be in phase and so, the circumference of an orbit must equal to the integral multiple of the wavelength i.e $2\pi r = n\lambda$. Substituting for wave length, in the de Broglie equation,

$$2\pi \mathrm{r} = \mathrm{n}\frac{\mathrm{h}}{\mathrm{p}} \text{ or } 2\pi \mathrm{r} = \mathrm{n}\frac{\mathrm{h}}{\mathrm{mv}} \text{ or } \mathrm{mvr} = \mathrm{n}\,\mathrm{x}\frac{\mathrm{h}}{2\pi}$$

Hence the angular momentum of electron (mvr) is an integral multiple of a constant ($h/2\pi$).

Exercise 1: Does, de Broglie hypothesis has any relevance to macroscopic matter?

de Broglie relation can be applied to both microscopic and macroscopic. Taking for example a macro sized 100Kg car moving at a speed of 100m/s, will have a wavelength of $\lambda = h/mv = 6.63\times10^{-30}$m while high energy γ-radiations have wavelength of only 10-12 m. Very small wavelength corresponds to high frequencies. Waves below certain wavelength or beyond certain frequencies undergo particle-antiparticle annihilation to create mass. So, wave nature or de Broglie wavelength is not observable in the macroscopic matter.

Exercise 2. If the velocity of the electron in this microscope is 1.6×10^6m/s, calculate de Broglie wavelength associated with this electron.

de Broglie Wavelength of $\lambda = h/mv = 4.55$Å

Heisenberg's uncertainty principle

Heisenberg's uncertainty principle is a key principle in quantum mechanics. In principle, it states that if we know **everything** about where a particle is located (**the uncertainty of position is small**), we know **nothing** about its momentum (the **uncertainty of momentum is large**), and vice versa. Versions of the uncertainty principle also exist for other quantities, such as energy and time. We discuss the momentum-position and energy-time uncertainty principles separately.

Momentum and Position

To illustrate the momentum-position uncertainty principle, consider a free particle that moves along the x-direction. The particle moves with a constant velocity u and momentum $p = mu$. As we know that according to de Broglie's relations, $p=\hbar k$ or $E=\hbar\omega$ and the one dimensional wave function for this particle is given by

$$\psi(x,t)=A[\cos(\omega t-kx)-i\sin(\omega t-kx)]=Ae^{-i(\omega t-kx)}=Ae^{-i\omega t}e^{ikx} \tag{26}$$

Also, the probability density function $|\psi(x,t)|^2=A^2$ is *uniform* and independent of time. The particle is equally likely to be found anywhere along the x-axis but has definite values of wavelength, wave number and therefore momentum. The uncertainty of position is infinite (completely uncertain about position) and the uncertainty of the momentum is zero (completely certain about momentum). This account of a free particle is consistent with Heisenberg's uncertainty principle.

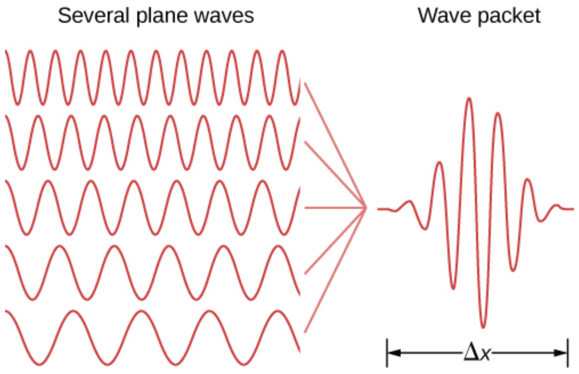


Figure 7 Superposition of several plane waves of different wavelengths produces a relatively localized wave.

Similar statements can be made of localized particles. In quantum theory, a localized particle is modeled by a linear superposition of free-particle (or plane-wave) states called a wave packet. An example of a wave packet is shown in figure (4). A wave packet contains many wavelengths and therefore by de Broglie's relations many momentum. This particle also has many values of position, although the particle is confined mostly to the interval Δx. The particle can be better localized (Δx can be decreased) if more plane-wave states of different wavelengths or momenta are added together in the right way (Δp is increased). According to Heisenberg, these uncertainties obey the relation that "the product of the uncertainty in position ($\boldsymbol{\Delta x}$) of a particle and the uncertainty in its momentum ($\boldsymbol{\Delta p}$) can never be less than one-half of the reduced Planck constant" mathematically

$$\Delta x\Delta p \geq \hbar/2 \tag{27}$$

This relation expresses Heisenberg's uncertainty principle. It places limits on what we can know about a particle from simultaneous measurements of position and momentum. If Δx is large, Δp is small, and vice versa. The Heisenberg uncertainty principle states that **it is impossible to know simultaneously the exact position and momentum of a particle. That is, the more exactly the position is determined, the less known the momentum, and vice**

versa. Heisenberg wrote "**Any use of the words 'position' and 'velocity' with accuracy exceeding that given by the uncertainty relation (equation 27) is just as meaningless as the use of words whose sense is not defined.**" Note that the uncertainty principle has nothing to do with the precision of an experimental apparatus. Even for perfect measuring devices, these uncertainties would remain because they originate in the wave-like nature of matter. The precise value of the product $\Delta x \Delta p$ depends on the specific form of the wave function. Interestingly, the Gaussian function gives the minimum value of the uncertainty product which is $\boldsymbol{\Delta x \Delta p = \hbar/2}$.

Exercise 1: Determine the minimum uncertainties in the positions of the following objects if their speeds are known with a precision of 1.0×10^{-3} m/s: (a) an electron and (b) a bowling ball of mass 6.0 kg.

Discussion: Given the uncertainty in speed $\Delta u = 1.0\times10^{-3}$ m/s, we have to first determine the uncertainty in momentum $\Delta p = m\Delta u$ and then invert equation (27) to find the uncertainty in position $\Delta x = \hbar/(2\Delta p)$.

Solution: For electron:

$$\Delta x = \frac{\hbar}{2\Delta p} = \frac{\hbar}{2m\Delta u} = 5.8\ cm$$

For bowling ball:

$$\Delta x = \frac{\hbar}{2\Delta p} = \frac{\hbar}{2m\Delta u} = 8.8 \times 10^{-33}\mathrm{m}$$

Conclusion / Significance:

It interesting to note that unlike the position uncertainty for electron, the position uncertainty for the bowling ball is immeasurably small. Planck's constant is very small, so the limitations imposed by the uncertainty principle are not noticeable in macroscopic systems such as a bowling ball.

Exercise 2: Estimation of the ground-state energy of a hydrogen atom using Heisenberg's uncertainty principle. (*Hint*: According to early experiments, the size of a hydrogen atom is ≈ 1 Å.)

Discussion:

An electron bound to a hydrogen atom can be modeled by a particle bound to a one-dimensional box of length L = 0.1nm. We know that the ground-state wave function of this system is a half wave. Which means, this is the largest wavelength that can "fit" in the box, so the wave function corresponds to the lowest energy state. We can take the average energy of a particle described by this function (E) as a good estimate of the ground state energy (E_0). This average energy of a particle is related to its average of the momentum squared, which is related to its momentum uncertainty.

Solution:

To solve this problem, we must be specific about what is meant by "uncertainty of position (Δx)" and "uncertainty of momentum (Δp)". For this particular case Δx means the possible space traveled by the electron in ground state of an atom defiantly it cannot exceed the size of an atom (L) which is supposed to be ≈ 1 Å. Then according to uncertainty principle Δp can be estimated as $\hbar/(2\Delta x)$. According to the theory of particle in a box the particle is assumed to be free particle i.e. the total energy of the particle is contributed by the kinetic energy only. Therefore the estimated ground state energy the H-atom is

$$E_0 = \frac{\Delta p^2}{2m} = \frac{\hbar^2}{8m\Delta x^2} = \frac{\hbar^2}{8mL^2} \cong 1\ eV\ (if\ L = 0.1\ nm)$$

Significance:

Based on early estimates of the size of a hydrogen atom and the uncertainty principle, the predicted ground-state energy of a hydrogen atom is in the eV range. Later on ionization energy of an electron in the ground-state energy is 13.6 eV, so this prediction is roughly confirmed.

Exercise 3: Prove that electrons cannot exist inside the nucleus.

Solution:

To prove it, let us assume that electrons exist in the nucleus. As the radius of the nucleus in approximately 10^{-14} m. If electron is to exist inside the nucleus, then uncertainty in the position of the electron is given by $\Delta x = 10^{-14}$ m.

According to uncertainty principle, $\boldsymbol{\Delta x \Delta p \geq \hbar/2}$ **thus** $\boldsymbol{\Delta p \approx \hbar/2\Delta x}$ = 1.05 x 10^{-20} kg m/ sec. If this is the uncertainty in the momentum of electron, then the momentum of electron should be at least of this order, that is p=1.05x10^{-20} kg m/sec. An electron having this much high momentum must have a velocity comparable to the velocity of light. Thus, its energy should be calculated by the following relativistic formula

$$\mathbf{E = (m_0^2\, c^4 + p^2 c^2)^{1/2} = 3.15\, x\, 10^{-12} J = 19.6\, x 10^6\, eV = 19.6\, MeV}$$

Therefore, if the electron exists in the nucleus, it should have an energy of the order of 19.6 MeV. However, it is observed that beta-particles (electrons) ejected from the nucleus during beta decay have energies of approximately 3 Me V, which is quite different from the calculated value of 19.6 MeV. Second reason that electron can not exist inside the nucleus is that experimental results show that no electron or particle in the atom possess energy greater than 4 MeV. Therefore, it is confirmed that electrons do not exist inside the nucleus.

Energy and Time

Another kind of uncertainty principle concerns uncertainties in simultaneous measurements of the energy of a quantum state and its lifetime, and given as

$$\boldsymbol{\Delta E \Delta t} \geq \frac{\hbar}{2} \tag{28}$$

where ΔE is the uncertainty in the energy measurement and Δt is the uncertainty in the lifetime measurement. The general meaning of the energy-time principle is that a quantum state that exists for only a short time cannot have a definite energy. The reason is that the frequency of a state is inversely proportional to time and the frequency connects with the energy of the state, so to measure the energy with good precision, the state must be observed for many cycles. To illustrate, consider the excited states of an atom. The finite lifetimes of these states can be deduced from the shapes of spectral lines observed in atomic emission spectra. Each time an excited state decays, the emitted energy is slightly different and, therefore, the emission line is characterized by a distribution of spectral frequencies (or wavelengths) of the emitted photons. As a result, all spectral lines are characterized by spectral widths. The average energy of the emitted photon corresponds to the theoretical energy of the excited state and gives the spectral location of the peak of the emission line. Short-lived states have broad spectral widths and long-lived states have narrow spectral widths.

Exercise 4: An atom typically exists in an excited state for about $\Delta t = 10^{-8}$s. Estimate the uncertainty Δf in the frequency of emitted photons when an atom makes a transition from an excited state with the simultaneous emission of a photon with an average frequency of $f = 7.1 \times 10^{14}$ Hz. Is the emitted radiation monochromatic?

Discussion:

We invert equation (28) to obtain the energy uncertainty $\Delta E \approx \hbar/2\Delta t$ and combine it with the photon energy $E=hf$ to obtain Δf. To estimate whether or not the emission is monochromatic, evaluate $\Delta f/f$.

Solution:

The spread in photon energies is $\Delta E = h\Delta f$. Therefore,

$$\Delta E = \frac{\hbar}{2\Delta t} \Rightarrow h\Delta f \approx \frac{\hbar}{2\Delta t} \Rightarrow \Delta f \approx 14\pi\Delta t = 14\pi(10^{-8}\mathrm{s}) = 8.0 \times 10^{6}\mathrm{Hz}$$

$$Now\ \frac{\Delta f}{f} = \frac{8.0 \times 10^{6}\mathrm{Hz}}{7.1\ \times\ 10^{14}\ \mathrm{Hz}} = 1.1 \times 10^{-8}$$

Significance:

Because the emitted photons have their frequencies within 1.1×10^{-6} percent of the average frequency, the emitted radiation can be considered monochromatic.

Corollary:

This problem can also justify the non-availability of two level laser. In this problem if we calculate the uncertainty in energy only it is approximately 66 neV. The physical meaning of the calculated uncertainty means the maximum possible change in the state of electron during the transition from one energy level to other i.e. the energy difference between the two energy level is 66neV which is extremely small energy that could be overcome by the free electron with its own kinetic energy. Hence the two states are not separated while they are continuum (actually separated but very closely spaced to each other). Therefore, lasing action or the condition of population inversion is not possible between the two energy level only.

Unsolved Problems

Problem 1: A sodium atom makes a transition from the first excited state to the ground state, emitting a 589.0-nm photon with energy 2.105 eV. If the lifetime of this excited state is 1.6×10−8s, what is the uncertainty in energy of this excited state? What is the width of the corresponding spectral line?

Problem2: (a) If the position of a chlorine ion in a membrane is measured to an accuracy of 5.00 μm, what is its minimum uncertainty in velocity, given its mass is 5.86×10^{-26} kg? (b) If the ion has this velocity, what is its kinetic energy in eV? (Compare this with typical molecular binding energies of about 5 eV.)

Problem 3: An ultrafast laser has a central wavelength of 550 nm. What pulse duration would result in a spread of wavelengths that just covered the visible spectrum, 400 nm to 700 nm?

Problem 4: A pion and a proton can briefly join together to form a delta particle. A measurement of the energy of the system shows a peak at 1236 MeV, corresponding to the rest energy of the delta particle, with an experimental spread of 120 MeV. What is the lifetime of the delta particle?

Problem 5: Does the Heisenberg uncertainty principle only apply to quantum physics? When you flip a coin, the outcome is uncertain. Does this arise from quantum uncertainty?

Problem 6: An electron and photon moving with speed 'v' and 'c', respectively have the same de Broglie wavelength. If the kinetic energy and momentum of an electron are E_e and P_e and that of a proton are E_{ph} and P_{ph} respectively, then show that ration Ee/Eph is c/2v.

Problem 7: Is the wavelength of electron on different orbits, same or different? If different what is the ratio of the wavelength in first and 4th orbit? (ans. (1/4)

Problem 8: Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit. (Hint. Start from Bohr Hypothesis i.e. $mvr = h/2\pi$, and use de Broglie concept to prove the result).

Physical interpretation of wavefunction

What is a wavefunction and Physical significance?

The wavefunction represented usually with the symbol Ψ, does not have any physical significance, while $|\Psi|^2 = \Psi^*\Psi$, signifies the probability of finding the particle. The Ψ is a complex quantity, it may assume positive or negative values and is not a measurable quantity. While $|\Psi|^2$ is a positive, real and measurable quantity.

All the wavefunctions representing a particle are needed to satisfy the **Normalization** condition. If a particle exists in the universe, the volume integral of the probability of finding the particle over the universe must be equal to 1, which is represented by

$$\int_{-\infty}^{+\infty} |\Psi|^2 \, dV = 1. \tag{1}$$

If $\int_{-\infty}^{+\infty} |\Psi|^2 \, dV = 0$, means the particle does not exist. Also the value of the integral never becomes negative, complex or infinity.

If the wavefunction satisfies the conditioned given in equation (1) , then the wavefunction is said to be normalised.

Well behaved wavefunction

In order to call a wavefunction, well behaved, it needs to satisfy the following conditions

1. Ψ must be continuous and single valued everywhere.
2. The partial derivatives $\partial\Psi / \partial x$, $\partial\Psi / \partial y$ and $\partial\Psi / \partial z$ must be continuous and single valued everywhere.
3. Ψ must be normalizable.

In order to make $\int_{-\infty}^{+\infty} |\Psi|^2 \, dV$, the third condition further requires that the wavefunction Ψ must go to zero when $x \rightarrow \pm\infty$, $y \rightarrow \pm\infty$ and $z \rightarrow \pm\infty$.

Generally, the probability of finding the particle within a region x_1 and x_2 is

$$P_{x_1,x_2} = \int_{x_1}^{x_2} |\Psi|^2 dx \, . \tag{2}$$

Example: Let $\Psi = \sin(2x)$ for a free particle. The probability of finding the particle between $x = 0.2$ and $x = 0.3$ is

$$P_{0.2,0.3} = \int_{0.2}^{0.3} |\sin(2x)|^2 dx = 0.023. \tag{3}$$

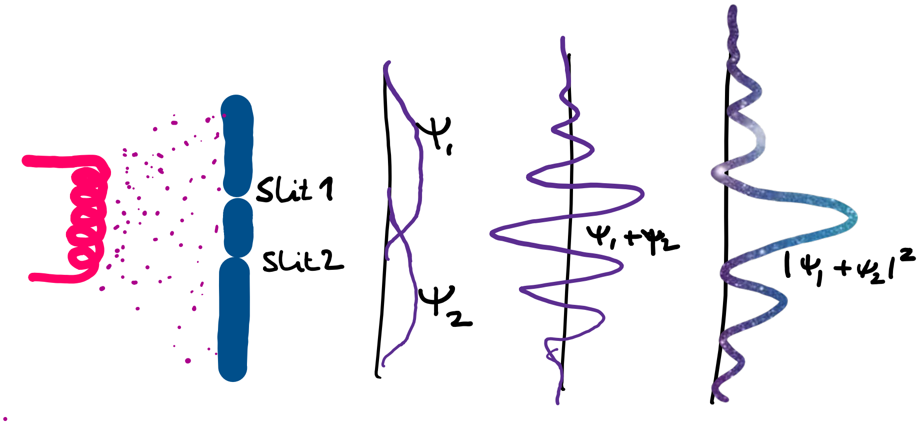
Properties of a wave function

All the wavefunction obey addition and subtraction rules like any other vector. If Ψ_1 and Ψ_2 represent the solution to a quantum mechanical system, then

$$\Psi = a_1\Psi_1 + a_2\Psi_2 \tag{4}$$

is also a solution to that system. a_1 and a_2 are constants. In other words the wavefunction obeys the principle of superposition.

In order to understand this, let us consider and example involving smaller particles such as electrons. Let the electrons are allowed to pass through the slits. A single isolated electron may pass through any one of the two slits. The wavefunctions Ψ_1 and Ψ_2 of an electron provides the probability of finding the electron through the slits 1 and 2, respectively as shown in the figure below.



In this case, the wavefunctions suggests the distribution of probable path of the electron to pass through each slit.

Operator associated with quantities	
Measurable parameter	**Operator**
Position (x)	x
Linear Momentum (p)	$-i\hbar\,{}^{\partial}/_{\partial x}$
Kinetic Energy (KE= $\boldsymbol{p^2}$ / $\boldsymbol{2m}$)	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
Potential Energy $(U(x))$	$U(x)$
Total Energy (E)	$i\hbar\,{}^{\partial}/_{\partial t}$
	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)$

Expectation Values

The wavefunction is expected to contain all the information about the particle or system under measurement. However, the physical quantities can not be measured directly. The value of the measurable quantity is obtained from the expectation values. The expectation value of a quantity G is obtained from the operator form of $\hat{G}$ as

$$\langle G \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{G} \psi \, dx \, . \qquad (4)$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

For example in order to measure the position x, the G is replaced with x as $\langle x \rangle = \int_{-\infty}^{+\infty} x|\psi|^2 \, dx$, the energy expectation value is obtained from $\langle E \rangle = i\hbar \int_{-\infty}^{+\infty} \psi^* \frac{\partial}{\partial t} \psi \, dx$ and the expectation value of momentum is found from $\langle p \rangle = -i\hbar \int_{-\infty}^{+\infty} \psi^* \frac{\partial}{\partial x} \psi \, dx$.

Example: The wavefunction of a particle in a potential well of width L is defined as $\psi = \sqrt{\frac{2}{L}} sin \frac{n\pi x}{L}$, find the expectation value of position.

The expectation value of position is defined as

$$\langle x \rangle = \int_{-\infty}^{+\infty} x|\psi|^2 \, dx = \frac{2}{L} \int_{-\infty}^{+\infty} x \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{2}{L}\left[\frac{x^2}{4} - \frac{x \sin\left(\frac{2n\pi x}{L}\right)}{\frac{4n\pi}{L}} - \frac{\cos\left(\frac{2n\pi x}{L}\right)}{8\left(\frac{n\pi}{L}\right)^2}\right]_0^L$$

$$= \frac{2}{L}\frac{L^2}{4} = \frac{L}{2}$$

Since the box has the dimension of L, the integration limit has been changed to 0 to L. Also the expectation value is found be equal to $L/2$, which means that the average position of the particle is at the middle of the box. It can be interpreted as the wavefunctions are symmetric in this case of a particle in a box. Hence the average position is at the middle of the box.

Question: Find the expectation values of $\langle E \rangle$, $\langle p \rangle$ and $\langle total\ energy \rangle$ in the above case.

Schrödinger’s Wave Equations

Introduction

The Schrödinger equation, is proposed by an Austrian physicist Erwin Schrödinger in 1925, describes the space- and time-dependence of quantum mechanical systems. It is of central importance to the theory of quantum mechanics, playing a role analogous to Newton's second law in classical mechanics. Hence, **Schrödinger’s equation itself is a law**.

> *Schrödinger’s equation cannot be derived from other basic principles of physics; it is a basic principle in itself.*

What is an Eigen equation?

An operator (say $\hat{O}$), when operated on a function (say $f(x)$) yields some λi times the function $f(x)$, it is called an eigen function represented by

$$\hat{O}f(x) = \lambda_i f(x). \tag{1}$$

Here, $\hat{O}$ is called ***eigen operator***, is called $f(x)$ ***eigen function***, λ_i is called ***eigen value***. Since the eigen function is reproduced, this equation is called as an ***eigen equation***. For example let $\hat{O} = \frac{d}{dx}$ and $f(x) = sin\,ax$, using equation (1) we can find

$$\frac{d}{dx}(sin\,ax) = a\,cos\,ax.$$

This is not a eigen equation and $f(x) = sin\,ax$ is not an eigen function of the operator $\hat{O}$. Let us consider a function $f(x) = Ae^{-ax}$, when operated on the operator $\hat{O} = \frac{d}{dx}$, *we obtain*

$$\frac{d}{dx}(Ae^{-ax}) = -aAe^{-ax}$$

Or

$$\hat{O}f(x) = -a\,f(x).$$

Accordingly, we can say that $f(x) = Ae^{-ax}$, is an eigen function of an operator $\hat{O}$, yielding an eigen value of -*a.*

Schrödinger equation from basic principles

In quantum mechanics the wave function ψ corresponds to the wave variable y of wave motion in general. However, ψ, unlike y, is not itself a measurable quantity and may therefore be complex. For this reason, we assume that ψ for a particle moving freely in the +*x* direction is specified by

$$\Psi = Ae^{-i(\omega t - kx)} \tag{2}$$

From the foundations of quantum mechanics such as de Broglie hypothesis, we shall write that

$$E = h\nu = \hbar\omega \text{ or } \omega = \frac{E}{\hbar} \tag{3}$$

and

$$\lambda = \frac{h}{p} \quad or \quad \frac{2\pi}{\lambda} = \frac{p}{\hbar} = k. \tag{4}$$

Using (3) and (4) in we rewrite the equation (2) as,

$$\Psi = Ae^{-(i/\hbar)(Et-px)}. \tag{5}$$

The equation (5) representing the wavefunction of a free particle moving in +*x* direction with total energy *E* and momentum *p*. The first and second order differentiation of the eq. (5) with respect to *x*, gives

$$\frac{\partial}{\partial x}\Psi = \frac{ip}{\hbar}\Psi \text{ and } \frac{\partial^2}{\partial x^2}\Psi = -\frac{p^2}{\hbar^2}\Psi. \tag{6}$$

The differentiation of (5) with time provides

$$\frac{\partial}{\partial t}\Psi = -i\frac{E}{\hbar}\Psi. \tag{7}$$

Equation (6) and (7) can be rewritten as

$$p^2\Psi = -\hbar^2\frac{\partial^2\Psi}{\partial x^2} \text{ and } E\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} \tag{8}$$

Classically, the total energy (*E*) of a free particle is written as

Total energy = kinetic energy + potential energy

$$E = \frac{1}{2}mv^2 + U = \frac{p^2}{2m} + U. \tag{9}$$

[1]Multiplying equation (9) by a wavefunction from right hand side Ψ

$$E\Psi = \frac{p^2}{2m}\Psi + U\Psi. \tag{10}$$

Substituting $E\Psi$ and $p^2\Psi$ from equation (8) in equation (10),

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U\Psi. \tag{11}$$

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[1] This is a too simple assumption to obtain Schrödinger equation. For accurate and more acceptable method refer to books on quantum mechanics.

The equation (11) obtained above is known as one-dimensional time-dependent Schrödinger’s equation. The equation shall be written for three-dimensional system as

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right) + U(x,y,z,t)\Psi. \tag{12}$$

The potential energy is a function of *x, y, z* and *t.* The value of potential energy *U*, if known could be used to solve the Schrödinger equation of a particle. The solution of Ψ could be used to predict the probability of finding the particle with respect *x, y, z* and *t.*

Time-independent or Steady state form

When the potential energy U of a particle does not depend explicitly with time t, it the Schrödinger equation can be simplified by removing all time dependent functions. The one-dimensional free particle wavefunction is rewritten as

$$\Psi = Ae^{-\left(\frac{i}{\hbar}\right)(Et-px)} = Ae^{-\left(\frac{iE}{\hbar}\right)t}e^{\left(\frac{ip}{\hbar}\right)x} = \psi e^{-\left(\frac{iE}{\hbar}\right)t} \tag{13}$$

Here, $\psi = Ae^{\left(\frac{ip}{\hbar}\right)x}$, is the time independent part of the wavefunction. Substituting the modified wavefunction (13) in the time-dependent Schrödinger equation (12),

$$-i\frac{E}{\cancel{\hbar}}i\cancel{\hbar}\psi e^{\cancel{-\left(\frac{iE}{\hbar}\right)}t} = -\frac{\hbar^2}{2m}e^{\cancel{-\left(\frac{iE}{\hbar}\right)}t}\frac{\partial^2\psi}{\partial x^2} + U\psi e^{\cancel{-\left(\frac{iE}{\hbar}\right)}t}.$$

After simplification,

$$E\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi.$$

Or

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-U)\psi = 0. \tag{14}$$

The equation (14) written above is popularly known as time-independent Schrödinger equation or Steady-state form of Schrödinger equation.

Questions:

1. Obtain time-dependent Schrödinger equation for a free particle from basic principles.
2. What is steady state form of Schrödinger equation?
3. Derive 3-Dimensional form of Schrödinger equation.

Solve the following

1. The time independent Schrodinger equation is:

(a) $\left[-\frac{h^2}{2m}\nabla^2 + V\right]\Psi = E\Psi$

(b) $-\frac{h^2}{2m}\nabla^2\Psi = E\Psi$

(c) $\left[-\frac{h^2}{2m}\nabla^2 + V\right]\Psi = i\hbar\frac{\partial\psi}{\partial t}$

(d) $\left[-\frac{h^2}{2m}\nabla^2 + (E-V)\Psi\right]\Psi = 0$

2. The wave function associated with a material particle is:
   (a) Only finite
   (b) Only continuous
   (c) Only single valued
   (d) Finite, continuous and single valued.
3. According to classical mechanics, which law(s) apply or applies to the behavior of macroscopic particles?
   (a) Newton's three laws
   (b) the differential wave equation
   (c) Dalton's law of multiple proportions
   (d) Kepler's Law
4. Schrodinger's equation described the
   (a) procedure for splitting an atom
   (b) complement of the wave function
   (c) behavior of "matter" waves
   (d) motion of light
5. The probability density is the
   (a) square root of the wave function
   (b) absolute value of the wave function
   (c) inverse of the wave function
   (d) absolute square of the wave function
6. The $\left|\Psi^2\right|$ represents:
   (a) probability density
   (b) charge density
   (c) energy density
   (d) intensity of wave
7. For normalization of wave function Ψ, the condition is:
   (a) $\int \Psi\Psi^* dx = 1$
   (b) $\int \Psi\Psi^* dx = 0$
   (c) $\int \Psi\Psi^* dx = \infty$
   (d) none of these
8. if $\int \Psi\Psi^* dx = 1$, the function Ψ is:
   (a) real
   (b) normalized
   (c) time independent
   (d) time dependent
9. If $\Psi = Ae^{-\alpha x^2/2}e^{iEt/\hbar}$ is a normalized wave function, the value of A will be :
   (a) 1
   (b) 0
   (c) $(\pi/\alpha)^{-1/4}$
   (d) $\alpha/2$
10. For Compton effect, the incident radiation must be in the :
    (a) Visible region
    (b) Infrared region
    (c) X-ray region
    (d) Ultraviolet region

Particle in a One-Dimensional Potential Well

By the end of this class, you will be able to:

- Describe how to set up a boundary-value problem for the stationary Schrödinger equation
- Explain why the energy of a quantum particle in a box is quantized
- Describe the physical meaning of stationary solutions to Schrödinger's equation and the connection of these solutions with time-dependent quantum states.
- Learn, how to adopt Schrödinger's equation to a realistic problem involving small particles and micro-nano system.

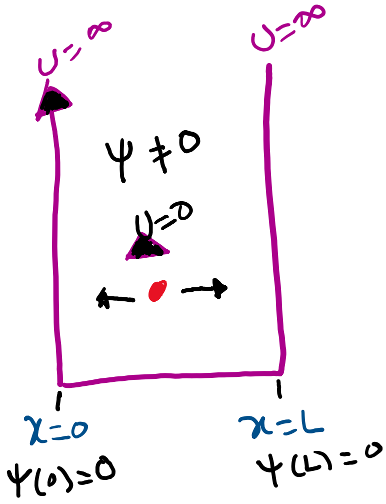
This problem is also known as **"Particle in a Box"**.

The Problem

The particle in a box problem is the simplest problem to solve using Schrödinger's equation.

- The problem assumes a particle is confined between two walls. *The wall* in turn, means the potential energy, hence it is called potential wall. Again for simplicity one-dimensional wall is assumed.
- Also, it is considered that the particle shall move inside the box between the walls. Hence the probability of finding the particle (a) on the wall and (b) outside the walls is zero.
- If assume the walls are located at $x = 0$ and at $x = L$, then the $\psi(0) = 0$ and $\psi(L) = 0$. These, conditions are known as boundary conditions for the 1-D potential well problem.

Solution to the Particle in a box or Particle in a potential well problem



As defined, the particle in a box problem assumes the potential energy of a particle inside the well is $U(x) = 0$ for $0 \leq x \leq L$, everywhere else it is infinity. A particle colliding on such walls would not lose its kinetic energy, also it can't penetrate through the walls.

The task is to find the wavefunction ψ for the particle within the limit of $0 \leq x \leq L$. Outside the box $\psi = 0$. Since the case does not require any time dependence, we will use the Schrodinger's steady state equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0 \tag{1}$$

Since $U(x) = 0$ for $0 \leq x \leq L$, the equation (1) will be rewritten as

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}E\psi=0. \tag{2}$$

The equation (2) is second differential equation and the solution is

$$\psi(x)=A\sin\frac{\sqrt{2mE}}{\hbar}x+B\cos\frac{\sqrt{2mE}}{\hbar}x. \tag{3}$$

A and B are two unknown constants. They may be found by applying the boundary conditions that at $x=0$, the wavefunction $\psi(0)=0$. This implies that

$$\psi(0)=A\times 0+B\times 1=0$$

Or $B = 0$.

The second boundary condition at $x=L$, the wavefunction $\psi(L)=0$, implies that

$$\psi(L)=A\sin\left(\frac{\sqrt{2mE}}{\hbar}L\right)=0.$$

Since A can not be equal to zero, we are left with $\sin(\frac{\sqrt{2mE}}{\hbar}L)=0$, or

$$\frac{\sqrt{2mE}}{\hbar}L=n\pi.$$

$$\Rightarrow E_n=\frac{n^2\pi^2\hbar^2}{2mL^2}. \tag{4}$$

Here n = 1, 2, 3, ….. . The equation (4) obtained for the particle energy E suggests that, the energy may have n number of quantised energy values represented as E_n. These energy values are called <u>energy eigen values of the particle in a 1-D potential well</u>.

The results obtained above are used to rewrite the equation (2) as

$$\psi_n(x)=A\sin\left(\frac{\sqrt{2mE_n}}{\hbar}x\right)=A\sin\left(\frac{n\pi x}{L}\right). \tag{5}$$

ψ_n will be now called as eigen function of the particle in 1D potential well. Further in equation only unknown is "A". In order to find the unknown constant A, we use the property of a well behaved wavefunction, that every eigen function must satisfy the property called "Normalization".

Accordingly, $\int_{-\infty}^{+\infty}|\psi_n(x)|^2\,dx=1$. However, the limits may be restricted to 0 and L,

$$\int_0^L\left|A\sin\left(\frac{n\pi x}{L}\right)\right|^2dx=1. \tag{6}$$

We will use the identity that $\sin^2(\theta) = \frac{1}{2}(1 - \cos 2\theta)$, in equation (6)

$$\frac{A^2}{2}\left[\int_0^L dx - \int_0^L \cos\left(\frac{2n\pi x}{L}\right) dx\right] = 1$$

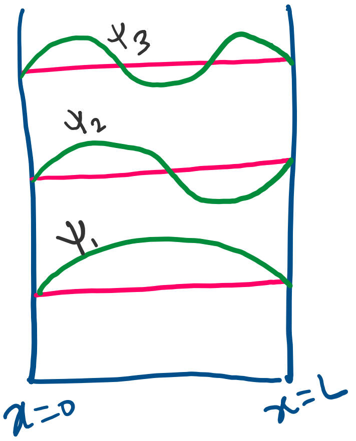
$$\frac{A^2}{2}\left[x - \frac{L}{2n\pi}\sin\left(\frac{2n\pi x}{L}\right)\right]_0^L = \frac{A^2}{2}L = 1$$

Or $A = \sqrt{\frac{2}{L}}$. The normalised wave function of the particle is

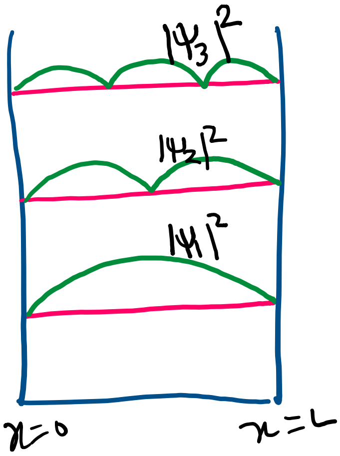
$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right). \qquad n = 1, 2, 3, \ldots \tag{7}$$

Understanding the wavefunction

The normalised wavefunction obtained in equation (7) are plotted for n = 1, 2 and 3. As expected from the boundary conditions the wavefunctions becomes zero in both extreme limits of x = 0 and x = L. For n = 2, 3 more zeros occur as well the values becomes negative. Since, ψ_n is the probability amplitude, it may have negative as well as imaginary values. The number of zero crossing occurs for n+1 times. The maximum amplitude the wave function can have is $\sqrt{\frac{2}{L}}$.



The probability finding the particle $|\psi_n(x)|^2$ for n = 1, 2 and 3 are plotted. All the probabilities are showing positive values only. The maximum value of the probability is $2/L$. For n = 1, the maximum probability of finding the particle lies at $x = L/2$, which is the center of the box. For n = 2, the maximum probability is found at two locations possible at $L/4$ and at $3L/4$.



Further, the particle with quantised wavefunction ψ_n as defined in equation (7) will have a quantised energy of E_n as defined in equation (4). This could be correlated with a string experiment, when more energy applied more loops are formed in the string. While for low applied energy the string shows less number of loops.

Questions

1. Find the probability that a particle trapped in a box L wide can be found between $0.25L$ and $0.35L$ for the ground and first excited states.
2. Find the expectation values of position, momentum and kinetic energy of a particle trapped in a box L wide.
3. The expectation value $\langle x \rangle$ of a particle trapped in a box L wide is $L/2$, which means that its average position is the middle of the box. Find the expectation value $\langle x^2 \rangle$.
4. Find the probability that a particle in a box L wide can be found between $x = 0$ and $x = L/n$ when it is in the n^{th} state.
5. A particle is in a cubic box with infinitely hard walls whose edges are L long. The wave functions of the particle are given by

   $$\psi = A \sin\frac{n_x \pi x}{L} \sin\frac{n_y \pi y}{L} \sin\frac{n_z \pi z}{L},$$

   with n_x, n_y, $n_z = 1, 2, 3, \ldots$. Find the normalization constant A.

   Hint: Solve $\int_0^L \int_0^L \int_0^L |\psi|^2 \, dxdydz = 1$.