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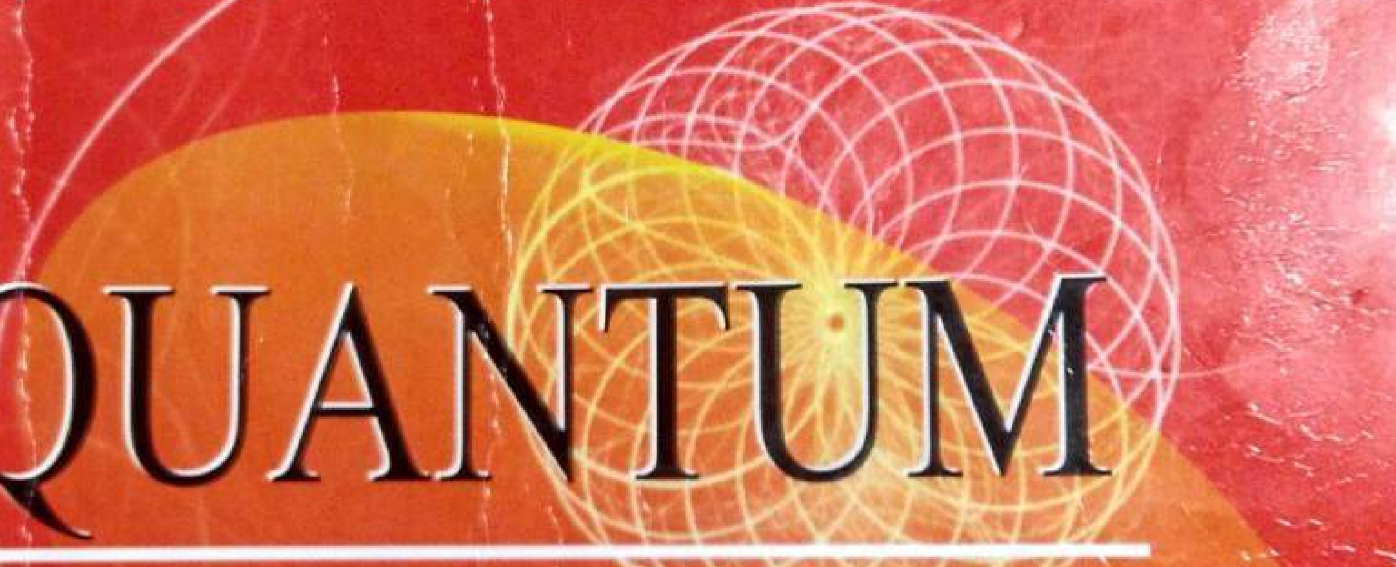

QUANTUM PHYSICS

H C Verma

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SURYA PUBLICATIONS, GHAZIABAD

To the Readers

If classical physics describes the world to be deterministic where the entire future course is predecided, quantum physics puts up a theory based on the assumption that the world is probabilistic where events take place on random chances. Yet there is no contradiction between the two and classical physics follows smoothly from quantum physics as the size of the system is taken to be reasonably large. Quantum physics is a beautiful subject having a rigorous mathematical foundation and at the same time has flavours of philosophy and many see different shades of spiritualism in it. It invites lots of abstract imagination but connects the events of the material world to the fantasies of imagination. It is a real thrilling experience to study quantum physics.

The guiding principle in writing this book had been to let the reader feel the excitement of understanding the new way of looking at the nature and correlate with the events occurring around. I presume this to be the first exposition of quantum physics for the reader after the Std XII level treatment of topics like Bohr's model of hydrogen atom, photoelectric effect, radioactivity etc. The treatment is based on sound mathematical formulation but the physical insight is not allowed to get lost in mathematical complexities. Relatively less common mathematical tools, especially operator algebra and related concepts like eigenvalue equations etc., are developed in detail before making use of them. I have made an effort to tell about the use of the theory developed in applications to physical phenomena in order to create an attachment towards the subject. That is why the title is *Quantum Physics* and not just *Quantum mechanics*.

The structure of the chapters includes the Text, Solved Problems and Exercises. A section called 'You learned in this chapter' after the text in each chapter gives the summary of the key concepts discussed in that chapter. The exercise questions at the end of a chapter are generally short and given to sharpen the understanding of the topics learned in the chapter and not to load the reader. In some of the chapters a section called 'Postscript' is appended which may be treated as an extension of the ideas dealt in that chapter. The Postscript material is generally not used in the later chapters and hence the completeness or continuity of the book is not affected if the Postscripts are left out in the first reading.

Though the book is written for any person having interest in Physics and looking for a learning material on quantum physics, it can be used as a textbook for a 40-50 hour course on basics quantum mechanics and applications.

The force behind writing this book had been my lively interactions with the students of Patna University and IIT Kanpur to whom I have given courses on quantum physics several times and have enjoyed the subject immensely. However the seeds of this book were probably sown by my teachers Dr A P Shukla and Dr Y R Waghmare at IIT Kanpur who taught me quantum physics in such a way that created a passion in me for this subject. The script of this book has been thoroughly read by Dr Devi Prasad Verma, Rtd Professor of Mathematics, who apart from suggesting editorial changes provided me vital feedback how a matured but nonphysicist person would respond to this writing. I also acknowledge the efforts of Mr Brajesh Pandey who has gone through the text and solved all exercise problems to ensure the correctness of answers. I am thankful to CDTE, IIT Kanpur for providing financial assistance to prepare the manuscript.

I have tried to keep errors away from this book to the best of my ability but I cannot ensure that it is error free. I will be grateful to all who communicate to me about any such error they come across. I will always look forward for suggestions to enhance the usefulness of this book.

Harish Chandra Verma

What is where?

Chapter 1 New Lessons from Young's Double-slit Experiment

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Chapter 4 Position and Linear Momentum of a Particle

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1

New Lessons from Young's Double-slit Experiment

1.1 The great wave–particle struggle

Seventeenth century. Very limited experimental facilities. But the nature and the natural phenomena were more or less the same as they are now. The sun shined during day time and darkness prevailed at night, lamps were needed to see things, mirrors used to show the image in the same way as they do now, rainbows had the same seven colours and so on. Certain behaviours of light were known to wise people.

(a) Light casts shadow showing that light travels in straight lines.

(b) Light is reflected from smooth surfaces. The rules of reflection are: (i) The incident ray, the reflected ray and the normal are in the same plane (ii) The angle of incidence is equal to the angle of reflection.

(c) When light travelling in a transparent medium enters another transparent medium, it bends unless it falls on the second medium normally. The rules of this phenomenon, called refraction, are: (i) The incident ray, the refracted ray and the normal are in the same plane (ii) If i and r be the angles of incidence and refraction respectively,

$$\frac{\sin i}{\sin r} = \mu_{2,1}$$

is constant for a given pair of media. For air to water, this constant is about 1.33 and for air to glass it is about 1.5. In general, when light goes from air to a solid or liquid medium it bends towards the normal.

(d) Light comes in different colours such as red, yellow, green, blue, violet, etc.

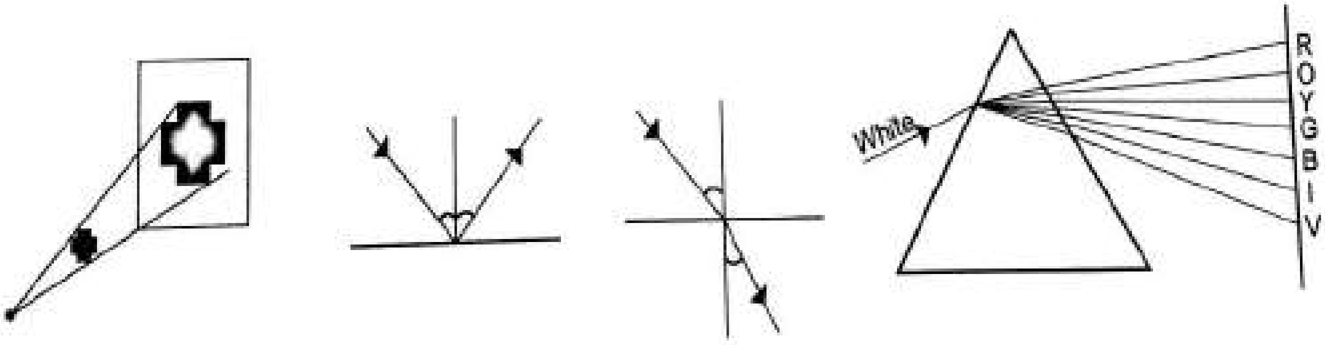

Fig. 1.1

Scientists were trying to understand why light shows these characteristic behaviours of straight line motion, reflection, refraction, colours, etc. Newton, who was respected by all who had interest i science, came out with what can be called "particle model of light". According to this model when yo put on a bulb, a candle or any other source of light, the source emits special kinds of particles—th particles of light. These particles were commonly called *corpuscles* and the description of light give by Newton, *corpuscle model of light*. The model was very simple in nature and was able to explain th observations available in those periods. Let us see how.

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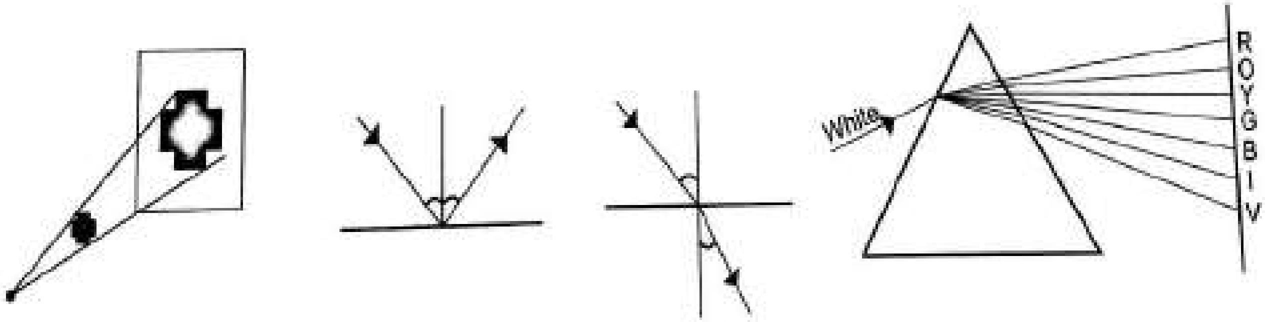

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Newton's first law of motion tells that every particle moves in a straight line with a constant speed if no force acts on it. So the particles of light should also move in straight lines in free space—a simple explanation for rectilinear motion of light.

Reflection is also simple to understand using the corpuscle model. A rubber ball hitting a smooth, hard surface rebounds. For a perfectly elastic oblique collision from a hard plane surface, the angle of incidence is equal to the angle of reflection, and the two velocity vectors and the normal to the surface are in the same plane. Similarly, a particle of light when strikes a smooth surface, say a mirror, reflects obeying the known laws of reflection.

If light goes from air to another transparent medium such as glass, the particles of the second medium attract the particles of light, resulting in deflection in their paths. Once the particle is well within the second medium, force is exerted on it from all sides. This makes the resultant force zero and the particle moves along a straight line. The deflection at the surface causes bending of the light ray. The force of attraction on the particles of light by the medium will also increase their speed and according to the Newton's model, speed of light in water or glass should be larger than that in air. However, in Newton's times there was no way to measure the speed of light in a medium and this prediction could not be verified.

To explain colours, Newton assumed that there are different types of particles of light, each corresponding to a particular colour.

Newton's theory, though very successful in understanding the known behaviour of light, did not go unchallenged. The Dutch physicist Christian Huygens, a contemporary of Newton, had a very different view. He suggested that light travels as a wave motion in a medium, more like a sound wave. When you put a source of light on, a disturbance is created in the equilibrium state of the medium. This disturbance travels in the medium. But then how does light cast shadow? A sound wave does not appear to cast shadow. If you put a cardboard between yourself and a source of sound, you still "hear" the sound quite well. This is because sound waves bend considerably at the edges of the cardboard. However, if you place the same cardboard between yourself and a source of light, you do not "see" the source. Huygens argued that the wavelength of light waves may be much smaller than the dimensions of the cardboard and other usual obstacles. In such a case the bending at the edges (diffraction) will be negligible and light will cast a sharp shadow.

The reflection or refraction of light can also be explained on the basis of wave theory. All waves, including sound waves, show these phenomena. Huygens proposed a way to construct the wavefronts and showed that the laws of reflection and refraction are the same for the waves as were known for light. However, if light were waves, the speed of light in water or glass should be less than that in air. This was in contrast to the prediction of corpuscle model. But there was no way to measure the speed of light in these media and hence it was not a deciding factor between the wave and corpuscle models.

There was an additional advantage with the wave theory. Different colours could be associated with different wavelengths of light. This was a much simpler description as compared to the case of Newton's corpuscle model where a large variety of particles had to be postulated, one for each colour.

At this stage all experimental observations about light could be explained by the corpuscle model of Newton and also by the wave model of Huygens. Thus it was a matter of choice for a person to favour one or the other model. Newton, enjoying a very high respect because of the great success achieved in the field of dynamics, had an advantage and the particle model of light by and large remained the popular choice for about 150 years.

1.2 Young's double-slit experiment settled the debate

Thomas Young in the year 1801 came out with an experiment which posed a serious challenge to the Newton's particle model of light. The experiment in its somewhat modified form is now performed in most of the school laboratories and is known as Young's double-slit experiment. I describe below the experimental arrangement, results obtained and their implications.

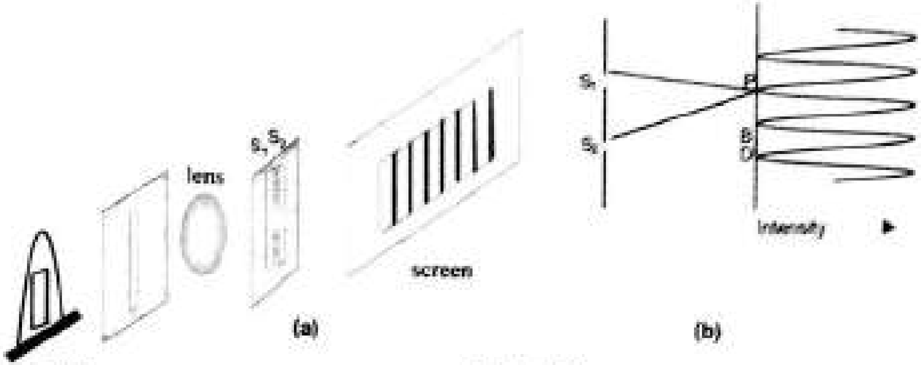

Fig. 1.2

Figure 1.2a shows schematically the experimental set up. Vertical narrow slits S$_1$ and S$_2$ are cut in an opaque plate. A monochromatic, parallel beam of light is allowed to fall on the slits. The light going through the two slits is collected on a screen placed on the other side of the slits. It is found that the intensity of light on the screen varies alternately between a maximum and a minimum value. If the two slits are identical, the minimum intensity is zero. What we visually see are bands of high and low intensities called bright and dark fringes. Figure 1.2b shows the cross-sectional view. The sinusoidal graph shows the variation of intensity on the screen. B and D are written for bright and dark corresponding to the positions of maximum and minimum intensity respectively. We can put a photographic plate in place of the screen and perform the experiment in a dark room, carefully avoiding stray lights. The film may later be developed to have a permanent record of bright and dark bands formed. Else, you can put up a photo sensitive screen and the intensity pattern can be stored in a computer system.

If you close one of the slits say S$_1$, the alternate bright and dark fringes disappear. The intensity is maximum at the central line from S$_2$ and decreases slowly as one moves away from this position (Figure 1.3a). Similar pattern is observed when S$_2$ is closed and S$_1$ is left open (Figure 1.3b).

Can Newton's particle model of light explain these observations? Consider a point P where dark fringe is formed when both the slits are open (Figure 1.2b). Why should the particles of light be so against reaching P? When only one slit is open, particles of light do reach P from this slit in good number (Figure 1.3). But when the other slit is "also" open they refuse to reach P. The particle model fails to explain this experimental observation.

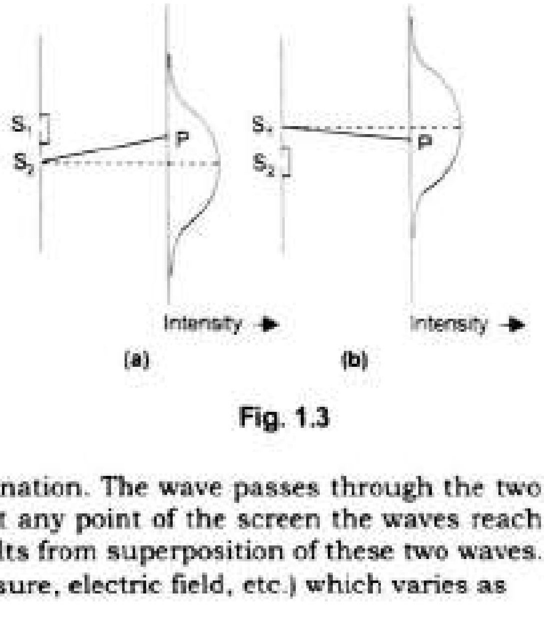

Fig. 1.3

On the other hand the wave model has a natural explanation. The wave passes through the two slits S$_1$ and S$_2$ together in the double-slit experiment and at any point of the screen the waves reach from both the slits. The varying intensity on the screen results from superposition of these two waves. A wave is described by some quantity Φ (displacement, pressure, electric field, etc.) which varies as

$$\Phi = \Phi_0 \sin(\mathbf{k}.\mathbf{r} - \omega t).$$

Φ_0 is called the wave amplitude and the intensity I_0 is proportional to its square. For a wave moving in x-direction

$$\Phi = \Phi_0 \sin(kx - \omega t).$$

Here $k = 2\pi/\lambda$ where λ is the wavelength, $\omega = 2\pi\nu$ where ν is the frequency and x is the distance from the source to the point of observation. When two waves

$$\Phi_1 = \Phi_0 \sin(kx - \omega t)$$

and
$$\Phi_2 = \Phi_0 \sin(kx - \omega t + \delta)$$

reach simultaneously at a point, the resultant value of Φ is

$$\Phi = \Phi_1 + \Phi_2 = \Phi_0 \left[\sin(kx - \omega t) + \sin(kx - \omega t + \delta)\right].$$

If $\delta = 0, 2\pi, 4\pi$, etc, i.e., an even multiple of π, the resultant amplitude is $2\Phi_0$ and the intensity is $4I_0$. On the other hand, if $\delta = \pi, 3\pi, 5\pi$, etc., i.e., an odd multiple of π, the resultant amplitude becomes zero making the intensity zero. As the two waves from S_1 and S_2 in the double-slit experiment cover different lengths to reach a point on the screen, a phase difference δ is introduced between them. Dark fringes are formed where δ is an odd multiple of π and bright fringes where it is an even multiple of π. In general, the intensity varies with δ as $I = 4I_0 \cos^2(\delta/2)$ where I_0 is the intensity when only one slit is open.

So, now there was an experiment which could only be understood by the wave model and not by the particle model. The particle model lost its superiority and the wave model got wide acceptance. A series of experiments performed in the nineteenth century further confirmed the wave nature of light. Fresnel and Fraunhofer demonstrated diffraction of light in conformity of wave character. Foucault could device a method to measure speed of light in laboratory in the year1850. Speed of light in glass and water came out to be smaller than that in air, contrary to the expectation from the particle model and consistent with the wave model. In the year 1860, Maxwell collected the known laws of electricity and magnetism, modified one of them (Ampere's law) and showed theoretically that a combination of electric and magnetic fields can travel in free space as a wave and when it does so, the speed of this wave is very close to 3×10^8 m/s. This happens to be identical with the measured speed of light. This not only established that light is a wave motion but also led us to know that light is an electromagnetic wave. This integrated the field of optics with that of electricity and magnetism. The wave quantity for light waves is written as **E** indicating electric field.

If particle model of light was dominant in seventeenth and eighteenth centuries, wave model had complete control in the nineteenth century.

1.3 Photoelectric effect reopened the issue

All was well with the wave theory of light and students were getting full marks for writing that light is a wave and not particles. The wave properties such as wavelength were measured using interference and diffraction experiments. People found that visible light (which is used to see objects) has wavelength in the range about 400 to 750 nm, violet having the shortest wavelength and red the longest. Electromagnetic waves with wavelength less than the visible range were termed as ultraviolet radiation and those with wavelength greater than this range as infrared radiation. Radiation was the general name for electromagnetic waves.

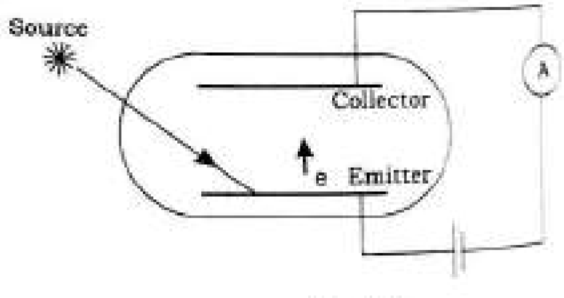

Fig. 1.4

Hallwachs in 1888 and Thompson in 1899 reported experiments which demonstrated that when ultraviolet radiation falls on a metal plate, electrons are ejected from the surface. For some metals, even visible light does the same. Lenard in 1902 studied carefully the dependence of number of electrons ejected and their kinetic energies on the wavelength of the incident light. And the results surprised everyone. The phenomena of emission of electrons on shining light on metallic surfaces is known as *photoelectric effect* and the electrons emitted in the process are called *photoelectrons*. An experimental set up is shown schematically in Figure 1.4 to study photoelectric effect. Electrons emitted by the lower metallic plate go to the collector plate and pass through the circuit to make a current. This current is called *photocurrent*. If you apply a negative potential (with respect to the emitter) to the collector, it will repel the electrons coming from the emitter. At a certain voltage no electrons will be able to reach the collector because of this repulsion and the current in the circuit will stop. This value of potential is called the *stopping potential*. At this potential, even the most energetic electron emitted from the emitter fails to reach the collector plate. The kinetic energy of such electrons is related to the stopping potential as

$$K_{max} = eV_{stopping} .$$

The main results related to photoelectric effect are as follows.

(a) Electrons are ejected from the metal almost instantaneously, say within $10^{-9}\,\mathrm{s}$, however weak be the source.

(b) For a given metal, there is a cut-off wavelength λ_0 such that a beam of light (radiation) of wavelength larger than λ_0 does not cause electrons to be ejected from the metal, however strong be the source.

(c) The maximum kinetic energy of the photoelectrons from a metal depends only on the wavelength of light and not on its intensity.

Can wave theory of light explain these observations? Emission of photoelectrons would not pose a problem. If an electron at the surface of a metal gets enough energy to resist attraction from the rest of the metal, it will come out. The minimum energy needed to detach an electron from the metal is called the *work function* Φ of the metal. The work function of typical metals is of the order of few electronvolts ($1\ \mathrm{eV} = 1.6\times10^{-19}\,\mathrm{J}$). Any wave carries energy and when it falls on a surface and gets absorbed, the energy is transferred to the surface. If light waves fall on a metal, they may give sufficient energy to an electron, enabling it to get ejected from the metal. But Lenard's quantitative observations posed problems for the wave theory.

Let us start with observation (a), i.e., near instantaneous emission of photoelectrons when appropriate light falls on a metal surface. If we use a very weak source of light, the energy transferred per unit time will be very small and it would take a long time before the electron can gather sufficient energy to come out. A straightforward calculation shows that in a typical experimental design, the time delay could be in seconds or even minutes. But the observation is different. However weak the source is, photoelectrons start coming out in time less than, say, a nanosecond.

Observation (b) is also not understandable on wave model. Why should there be any cut off wavelength? For any wavelength, light wave carries energy. If the source is strong, or we shine light for sufficiently long time, energy will be absorbed by the electrons in the metal and they should come out. But that is not the case and there is a sharp cut off wavelength λ_0. Even if λ is slightly greater than λ_0, no emission takes place however strong the source is and for whatever duration you shine the light.

Similarly, it is difficult to explain observation (c), i.e., why the maximum kinetic energy of photoelectrons is independent of intensity of the incident light. More intensity should mean deposition of more energy and that should mean more kinetic energy of the photoelectrons. But it is not so. Rather kinetic energy depends on the wavelength.

It turns out that the answer lies with the particle model of light. Albert Einstein in a way reverted to the particle model and explained all the observations of photoelectric effect. He proposed in 1905 that light should be thought of as a collection of "discrete" quanta, each having a particular amount of energy. You can count the quanta—one, two, three, —like any other particles. These quanta or particles are called *photons*. A stronger source means more number of photons getting emitted from it per unit time.

When light falls on a metal, photons get absorbed by the electrons. If one such photon can fall only on one electron, whole of its energy is transferred to the electron in one go. It is just like collision of two particles, the photon and the electron, and in no time the photon energy is transferred to the electron. If this energy is more than the work function, the electron is likely to be ejected. So photoelectric emission starts almost instantaneously, however weak is the source.

The other two observations listed can be explained if we assume that the energy of a photon depends on the wavelength of the light and that a photon corresponding to light of wavelength λ has energy

$$E = \frac{hc}{\lambda} \tag{1.1}$$

where h is a universal constant having value 6.626×10^{-34} J s (correct to four significant digits) and c is the speed of light 29,97,92,458 m/s (in vacuum). The constant h is called *Planck's constant* after the great physicist Max Planck who contributed a lot in the development of quantum mechanics. The value of hc may be written approximately as 1240 eV nm. The cut-off wavelength (also known as threshold wavelength) λ_0 for a given metal is related to its work function Φ as

$$\Phi = \frac{hc}{\lambda_0}. \tag{1.2}$$

Equations 1.1 and 1.2 tell that if $\lambda > \lambda_0$, you will have $E < \Phi$ and the photon energy will not be sufficient to eject an electron out of the metal. If you use a source of higher intensity, you are only sending more photons per unit time. But the energy of each photon remains less than the work function and the electron does not come out in any of these photon-electron collisions. You may ask why two or more photons cannot hit simultaneously a single electron and bring it out. They can, but the probability of such an event is extremely small and we do not observe it in experiments. For $\lambda < \lambda_0$, you have $E > \Phi$ and the electron, getting energy E from the photon, can come out of the metal. This explains the existence of a cut-off wavelength.

An electron receiving energy E from a photon may loose a part of it inside the metal by interaction with ions or other electrons before coming out of the metal. If it does not suffer any such energy loss, its kinetic energy, when it comes out of the metal, would be the maximum possible and I denote it by $K_{\max}$. Thus,

$$K_{\max} = \frac{hc}{\lambda} - \Phi \tag{1.3}$$

which depends on the wavelength but not on the intensity of the source of light.

Einstein got Nobel Prize for his explanation of photoelectric effect on the basis of photon picture. There are many experiments where light shows up as photons, each photon having a definite energy and also a definite momentum. While applying the principles of conservation of energy and momentum you must include the photons wherever these are involved in the interaction.

What is the nature of light then? Young's double-slit experiment shows that light must be waves as they interfere to produce bright and dark fringes which particles cannot do. Photoelectric effect shows that light must be particles as waves cannot transfer a finite amount of energy almost instantaneously. Does it mean light changes its character depending on which particular experiment you are doing?

1.4 Light is wave as well as particle

I just discussed that for a proper understanding of the photoelectric effect one must assume that light falls on the metal as a stream of discrete photons, each photon having a definite energy and momentum. But can we forget the wave character of light altogether to understand this experiment? No, the photon energy depends on the "wavelength". Where does the idea of wavelength come from? Even in photoelectric effect, light has not forgotten its wave character. Though it presents itself to the metal as discrete photons, explanation of cut off wavelength and kinetic energy of the photoelectrons do need wave aspect to be retained. A proper explanation of photoelectric effect needs both, the wave and the particle characters of light.

Well and good. But how about the Young's double-slit experiment? This experiment had put the wave theory on top. Does Young's double-slit experiment also need the particle aspect of light for its proper explanation? Yes, it does. Let me show how.

Suppose you use a very weak source of light in the double-slit experiment and a device such as a photographic film to permanently record the interference pattern as the screen. Switch on the light source for a very short time and develop the film. What you see is a few random dots on the film here and there and not a faint interference pattern as may be expected from the wave description of light. Light strikes the film as separate events of collision, showing its photon character. What happens if you increase the exposure time? As you allow the experiment to run for a somewhat longer period, many more dots appear on the film. At some stage, you will start identifying the interference pattern. Dots appear in larger number where the wave theory predicts constructive interference and few dots appear where it predicts destructive interference. If you run the experiment for long enough time, you don't observe dots as they merge with each other and the usual bright and dark fringes are seen.

All this may look a hypothetical experiment, but with modern technology using highly sensitive CCD camera, such experiments are performed very commonly.

So the fringe pattern in Young's double-slit experiment is actually formed from the photons striking the screen one by one. Particle picture has to be retained to properly understand the interference experiment. But the wave picture is equally important. The number of photons reaching a particular place on the screen is proportional to the intensity of the resultant wave obtained by superposition of the individual waves taking care of "phase difference". The intensity at the central point is four times what it would have been if only one slit is open. Thus if each slit sends N photons when the other is closed, the two together send $4N$ photons at the central point. Similarly, at the points of destructive interference, each slit sends N photons if the other is closed. But when both slits are open, they together send no photon at such points. Remember, you can use a very weak source so that photons are emitted one by one and presence of two photons near the slits is unlikely. It is not the interaction between the photons that is changing the situation. The fate of a single photon depends on whether one slit is open or both are open. And this fate is governed by the electromagnetic wave that obeys wave equations.

Though the screen receives light only in discrete quanta, i.e., photons, and also the source emits light only as photons, an electromagnetic wave is always associated with light. Light is both wave and particle. Where the photon will land and where not, is governed by the electric field $\mathbf{E}$ which travels as a wave which interferes and diffracts like any other wave.

Please do not think photon and electromagnetic wave as two different entities existing separately. It is the same entity we call light which shows up as photons on the screen and waves on the slits.

1.5 A new way to think

The above discussion on the nature of light may have left you in a confused state. This is because you have been accustomed to think in certain ways. The experimental findings described above tell that there are new lessons which may not be consistent with "common sense". Let me state them in more ordered fashion.

(a) An object like light has both particle and wave character at the same time (*dual nature*). Whenever you detect light you only detect it as a photon (particle), having a very small spatial extent, a definite energy and a definite linear momentum. But the probability that a photon is found at a given place, is governed by a wave that has a definite wavelength λ and a definite frequency ν.

(b) Young's double-slit experiment with short exposure gives some random impacts on the screen. Suppose you repeat the experiment in identical conditions—same source, same geometry, same time of exposure—changing only the photographic plate. Both the films have bright dots. If you put one film over the other, you don't get a dot over a dot. The two patterns are not identical. This observation has a very important lesson to teach—*identical* *experiments need not give identical results.* In other words, it is not always possible to tell beforehand what the result of a proposed experiment will be. No theory tells you where a photon incident on a double-slit will land up on the screen. Theory only gives the probabilities of different possible locations where the photon may reach. Only when a large number of photons go through the double-slit, you start seeing the intensity distribution matching with the theoretical predictions.

(c) The location of a photon described by the electric field $\mathbf{E} = \mathbf{E}_0 \cos(\mathbf{k}.\mathbf{r} - \omega t)$ is indefinite. The probability of its being found at position $\mathbf{r}$ at a given time t is proportional to $|\mathbf{E}_0|^2$ which is nonzero in a large region (in principle from $-\infty$ to ∞). But the moment we "detect" it, by reaction with sodium bromide molecule or by interaction with retina, it gets localized in a small region. The measurement process drastically changes the condition of the photon. We conclude that *measurement disturbs the system in a fundamental fashion.*

1.6 Relation between wave and particle parameters

A wave is characterized by parameters like wavelength λ, frequency ν, wave vector $\mathbf{k}$, etc. The direction of the wave vector $\mathbf{k}$ gives the direction of propagation of the wave. The magnitude $k = |\mathbf{k}|$ is related to the wavelength λ as $k = 2\pi/\lambda$.

The particle parameters are energy and momentum. For a photon, the energy is related to the frequency as

$$E = h\nu = \hbar\omega. \tag{1.4}$$

Here $\hbar$ is written for $h/2\pi$ and the angular frequency ω is equal to $2\pi\nu$. Equation 1.4 is also known as the Einstein relation. The photon also has a momentum p which is related to the wavelength λ as,

$$p = h/\lambda = \hbar k \tag{1.5}$$

or,

$$\mathbf{p} = \hbar\mathbf{k} \tag{1.6}$$

where $\mathbf{p}$ is the linear momentum vector and $\mathbf{k}$ is the wave vector.

For photons, the energy and momentum are related as $E = pc$. Using this, $E = hc/\lambda$.

1.7 You learned in this chapter

- For an adequate understanding of the behaviour of light, one has to retain both particle and wave pictures.
- Light is always detected as discrete particles called photons.
- Continuous looking interference patterns are built up from individual impact of photons.
- The probability of finding a photon at a particular place is governed by an electromagnetic wave and is proportional to the square of the amplitude of the wave.
- The energy and linear momentum of a photon are related to the wavelength and the frequency of the associated electromagnetic wave as

$$E = \hbar\omega = \frac{hc}{\lambda}, \ \mathbf{p} = \hbar\mathbf{k}, \ |\mathbf{k}| = \frac{2\pi}{\lambda}.$$

- Photoelectric effect is well described by assuming that one photon interacts with one electron at a time and transfers whole of its energy to the electron.
- An experiment repeated in identical conditions may give different results. Laws of physics only give the probabilities of different possible results.
- Measurement on a system can disturb its state drastically.

Solved Problems

1. The wavelength of light coming from a sodium vapour lamp is close to 589 nm. Find the energy of a photon corresponding to this wavelength.

Solution: The energy of a photon is related to the wavelength as $E = \frac{hc}{\lambda}$. The value of hc is

$$hc = (6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (3.0 \times 10^{8}\,\mathrm{m\,s^{-1}})$$
$$= \frac{6.626 \times 10^{-34}\,\mathrm{eV\,s}}{1.6 \times 10^{-19}} \times (3.0 \times 10^{8}\,\mathrm{m\,s^{-1}}) = 1240\ \mathrm{eV\,nm}.$$

So, $$E = \frac{1240\ \mathrm{eV\,nm}}{589\ \mathrm{nm}} = 2.1\,\mathrm{eV}.$$

2. What is the linear momentum of a photon of radiation having electric field described by $\mathbf{E} = E_0\hat{i}\cos\left[k_0(y+z) - \omega t\right]$? What is its magnitude?

Solution: The equation for the electric field of an electromagnetic wave can be written as

$$\mathbf{E} = \mathbf{E}_0 \cos(\mathbf{k}\cdot\mathbf{r} - \omega t).$$

You can write the given equation in this form. Thus,

$$\mathbf{E} = E_0\hat{i}\cos\left[\left(k_0\hat{j} + k_0\hat{k}\right)\cdot\left(x\hat{i} + y\hat{j} + z\hat{k}\right) - \omega t\right] = E_0\hat{i}\cos(\mathbf{k}\cdot\mathbf{r} - \omega t)$$

where $\mathbf{k} = k_0\hat{j} + k_0\hat{k}$ and $\mathbf{r} = x\hat{i} + y\hat{j} + z\hat{k}$.

The linear momentum of the photon is

$$\mathbf{p} = \hbar\mathbf{k} = \hbar\left(k_0\hat{j} + k_0\hat{k}\right)$$

The magnitude of the linear momentum is

$$|\mathbf{p}| = \hbar\left|k_0\hat{j} + k_0\hat{k}\right| = \sqrt{2}\hbar k_0.$$

3. What is magnitude of the linear momentum of a photon in a beam of He-Ne laser $(\lambda = 634\,\mathrm{nm})$? Express your answer is eV/c.

Solution: $$p = \frac{h}{\lambda} = \frac{hc}{\lambda c}$$
$$= \frac{1240\,\mathrm{eV\,nm}}{(634\ \mathrm{nm})c} = 1.96\ \mathrm{eV}/c.$$

4. A beam of light of wavelength 420 nm has the same intensity as another beam of light of wavelength 630 nm. The first beam, falling perpendicularly on a certain area of a wall, deposits 12×10^{16} photons per second per square centimeter of the wall. How many photons will the second beam deposit per second per square centimetre of a wall on which it falls perpendicularly.

Solution: The intensity of a wave is defined as the total energy falling per unit area per unit time on a perpendicular cross-section. Thus both the beams will deposit same amount of energy on the one square centimeter area of the wall in one second. osited by the first beam, the corresponding energy deposited is

$$E = n_1\left(\frac{hc}{\lambda_1}\right).$$

Similarly if n_2 is the number of photons deposited by the second beam,

$$E = n_2\left(\frac{hc}{\lambda_2}\right).$$

Thus $$\frac{n_1}{\lambda_1} = \frac{n_2}{\lambda_2}$$

or, $$\frac{12\times10^{16}}{420} = \frac{n_2}{630}$$

or, $$n_2 = \frac{630}{420}\times12\times10^{16} = 18\times10^{16}.$$

5. An electron moving with a speed 2c/511 hits a positron at rest. The two particles annihilate each other and two photons are emitted in exactly opposite directions. Find the energies of these photons. Mass of the electro = Mass of the positron = 511 keV/c^2.

Solution: The speed of the electron is $2c/511$ which is much smaller than the speed of light in vacuum. Hence I can use non relativistic equations. The rest mass energy of the electron-positro pair is

$$2m_ec^2 = 2\times\left(511\frac{\text{keV}}{c^2}\right)c^2 = 1022\text{ keV}.$$

The kinetic energy of the electron is

$$\frac{1}{2}m_e\upsilon^2 = \frac{1}{2}\left(511\frac{\text{keV}}{c^2}\right)\times\left(\frac{2}{511}c\right)^2$$

$$= \frac{2}{511}\text{keV}.$$

The total energy is $2m_ec^2 + \frac{1}{2}m_e\upsilon^2$.

The net linear momentum is $m_e\upsilon = \left(511\frac{\text{keV}}{c^2}\right)\left(\frac{2c}{511}\right) = 2\text{ keV}/c$.

Figure 1W.1 shows the situation before and after the annihilation. The photons are moving in exactly opposite directions. To conserve momentum, the photons must move along the same direction as that of the initial velocity of the electron.

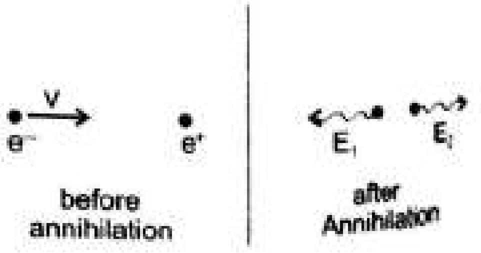

Fig. 1W.1

Let the energies of the two photons be E_1 and E_2. From conservation of energy,

$$E_2 + E_1 = 2m_ec^2 + \frac{1}{2}m_e\upsilon^2 \quad (i)$$

The linear momentum of a photon is

square centimeter area of the wall in one second. If n_1 is the number of photons deposited by the first beam, the corresponding energy deposited is

$$E = n_1\left(\frac{hc}{\lambda_1}\right).$$

Similarly if n_2 is the number of photons deposited by the second beam,

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The total energy is $2m_ec^2 + \frac{1}{2}m_e\upsilon^2$.

The net linear momentum is $m_e\upsilon = \left(511\frac{\text{keV}}{c^2}\right)\left(\frac{2c}{511}\right) = 2\text{keV}/c$.

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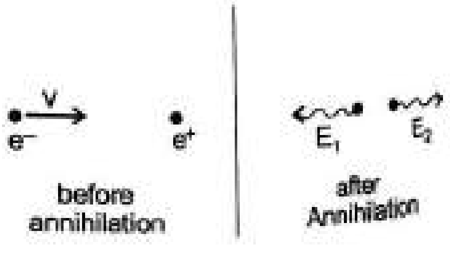


Fig. 1W.1

Let the energies of the two photons be E_1 and E_2. From conservation of energy,

$$E_2 + E_1 = 2m_ec^2 + \frac{1}{2}m_e\upsilon^2 \quad \text{(i)}$$

The linear momentum of a photon is

$$p = \frac{h}{\lambda} = \frac{hc}{c\lambda} = \frac{E}{c}.$$

Thus, from conservation of linear momentum,

$$\frac{E_2}{c} - \frac{E_1}{c} = m_e \upsilon$$

or, $E_2 - E_1 = m_e \upsilon c$ (ii)

From (i) and (ii)

$$E_1 = \frac{1}{2}\left[2m_e c^2 + \frac{1}{2}m_e \upsilon^2 - m_e \upsilon c\right]$$

$$= m_e c^2 + \frac{1}{4}m_e \upsilon^2 - \frac{1}{2}m_e \upsilon c$$

and $E_2 = \frac{1}{2}\left[2m_e c^2 + \frac{1}{2}m_e \upsilon^2 + m_e \upsilon c\right]$

$$= m_e c^2 + \frac{1}{4}m_e \upsilon^2 + \frac{1}{2}m_e \upsilon c$$

Putting the values,

$$E_1 = 511\,\text{keV} + \frac{1}{511}\,\text{keV} - 1\,\text{keV} \approx 510\,\text{keV}$$

$$E_2 = 511\,\text{keV} + \frac{1}{511}\,\text{keV} + 1\,\text{keV} \approx 512\,\text{keV}$$

6. A beam of 450 nm light is incident on a metal having work function 2.0 eV placed in a magnetic field B. The most energetic electrons, emitted perpendicular to the field, are bent in circular arcs of radius 20 cm. Find the value of B.

Solution: The kinetic energy of the most energetic electrons is

$$K = \frac{hc}{\lambda} - \varphi$$

$$= \frac{1240\,\text{eV nm}}{450\,\text{nm}} - 2.0\,\text{eV}$$

$$= 0.76\ \text{eV} = 1\cdot 2 \times 10^{-19}\,\text{J}.$$

The linear momentum $= mv = \sqrt{2mK}$

$$= \sqrt{2 \times \left(9\cdot 1 \times 10^{-31}\,\text{kg}\right) \times \left(1\cdot 2 \times 10^{-19}\,\text{J}\right)}$$

$$= 4\cdot 67 \times 10^{-25}\,\text{kg m/s}.$$

When a charged particle is sent perpendicular to a magnetic field, it goes along a circle of radius

$$r = \frac{mv}{qB}.$$

Thus, $$0\cdot 20\,\text{m} = \frac{4\cdot 67\times 10^{-25}\,\text{kg m/s}}{\left(1\cdot 6\times 10^{-19}\text{C}\right)\times B}$$

or, $$B = \frac{4\cdot 67\times 10^{-25}\,\text{kg m/s}}{\left(1\cdot 6\times 10^{-19}\text{C}\right)\times (0\cdot 20\,\text{m})} = 1\cdot 46\times 10^{-5}\,\text{T}.$$

7. The work function of a metal is $2.0\times 10^{-19}\,\text{J}$. (a) Find the threshold frequency for photoelectric emission. (b) If the metal is exposed to a light beam of frequency $6.0\times 10^{14}\,\text{Hz}$, what will be the stopping potential?

Solution: **(a)** The threshold frequency ν_0 is related to the work function Φ as $h\nu_0 = \Phi$. So,

$$\nu_0 = \frac{\Phi}{h} = \frac{2.5\times 10^{-19}\,\text{J}}{6.6\times 10^{-34}\,\text{Js}} = 3.8\times 10^{14}\,\text{s}^{-1}.$$

(b) The energy of a photon is related to the frequency as $E = h\nu$. For the frequency given in the problem, the photon energy is

$$E = (6.6\times 10^{-34}\,\text{J s})\times(6.0\times 10^{14}\,\text{s}^{-1}) = 3.9\times 10^{-19}\,\text{J}.$$

The maximum possible kinetic energy of the photoelectrons is

$$(3.9\times 10^{-19}\text{J}) - (2.0\times 10^{-19}\text{J}) = 1.9\times 10^{-19}\,\text{J} = \frac{1.9\times 10^{-19}}{1.6\times 10^{-19}}\,\text{eV} = 1.2\,\text{eV}.$$

Thus the stopping potential is 1.2 V.

8. The light emitted by a 1 mW He-Ne laser source is attenuated by a factor of 10^{11} by passing it through an attenuator. The attenuated light is sent into an aluminum box of length 80 cm. How many photons do you expect in the box at any given instant of time?

Solution: The energy sent by the source-attenuator system into the tube is $1\,\text{mW}\times 10^{-11} = 10^{-14}\,\text{J}$ per second. Remembering that the wavelength of He-Ne laser is 633 nm, the energy of each photon is

$$E = \frac{1240\,\text{eV nm}}{633\,\text{nm}} = 1.96\,\text{eV} = 3.1\times 10^{-19}\,\text{J}.$$

The number of photons entering the tube per second is therefore,

$$n = \frac{10^{-14}\,\text{J}}{3.1\times 10^{-19}\,\text{J}} = 3.23\times 10^{4}.$$

The time taken by light to cover the 80 cm of length in the tube is

$$t = \frac{80\,\text{cm}}{3.0\times 10^{8}\,\text{m/s}} = 2.67\times 10^{-9}\,\text{s}.$$

At any given time the number of photons in the tube is the same as that entering the tube in $2.67\times 10^{-9}\,\text{s}$. This number is

$$n\,t = (3.23\times 10^{4})\times(2.67\times 10^{-9}) \approx 10^{-5}.$$

So not more than one photon is expected in the tube at any given instant of time.

EXERCISES

1. Find the linear momentum of a photon of X-rays of wavelength 1 angstrom in keV/c. **Ans.** 12.4 keV/c
2. What is the energy of a photon corresponding to the wavelength 654 nm? Light of this wavelength is emitted by hydrogen gas when electric current is passed through it at appropriate pressure. **Ans.** 1.90 eV
3. How many photons are emitted per second by a 1 mW He-Ne laser? What is the average time interval between emission of successive photons? **Ans.** $3.23 \times 10^{15}, 3.1 \times 10^{-16}$s
4. An electromagnetic wave has magnetic field given by $\mathbf{B} = \mathbf{B}_0 \sin 2\pi \left[\frac{x}{124 \text{ nm}}\right]$ at time $t = 0$. Find the linear momentum of a photon in this beam. **Ans.** 10eV/c
5. It is found that the maximum wavelength of radiation that can cause photoelectric effect from lithium is 497 nm. What is the work function of Lithium? **Ans.** 2.5 eV
6. In an experiment with photoelectric effect, it was found that the stopping potential decreases from 1.85 V to 0.82 V as the wavelength of the incident light is varied from 300 nm to 400 nm. Calculate the value of the Planck's constant from this data. **Ans.** 6.6×10^{-34} Js
7. The electric field associated with a light beam is given by $E = E_0 \sin[(1.57 \times 10^7 \text{ m}^{-1})(x - ct)]$. Find the maximum kinetic energy of the photoelectrons if this beam falls on a metal having work function 1.9 eV. **Ans.** 1.2 eV
8. Data are recorded during experiments on photoelectric effect in a photo cell. A number of experiments are performed using lights of different colours and cathodes of different metals. The quantities recorded are applied voltage, intensity of light, photo current, wavelength of light, stopping potential. A student plots the variation between two of the observed quantities but does not label them. The plot has the shape shown in the figure. What can be the quantity represented on the horizontal axis?

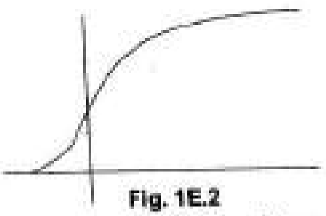


Fig. 1E.2

Ans. Photocurrent, applied voltage

9. A point source of monochromatic light of 1·0 mW is placed at a distance of 5.0 m from a metal surface. Light falls perpendicularly on the surface. Assume wave theory of light to hold and also that all the light falling on the circular area with radius $= 1 \cdot 0 \times 10^{-9}$m (which is few times the diameter of an atom) is absorbed by a single electron on the surface. Calculate the time required by the electron to receive sufficient energy to come out of the metal if the work function of the metal is 2.0 eV. **Ans.** 8.8 hours
10. A light beam of wavelength 400 nm is incident on a metal plate of work function 2.20 eV. (a) A particular electron absorbs a photon and makes two collisions before coming out of the metal. Assuming that 10% of the energy excess of the average energy of other electrons is lost to the metal in each collision, find the kinetic energy of this electron as it comes out of the metal. (b) Under the same assumption, find the maximum number of collisions the electron can suffer and still be able to come out of the metal. **Ans.** (a) 0.31 eV (b) 3
11. Consider the light beam coming from a 1mW He-Ne laser source. How many photons are there in 1 meter length of the beam? **Ans.** 1.08×10^7
12. Light from a 1 mW He-Ne source is attenuated by a factor of 10^{11}. Estimate the minimum distance between the photons. **Ans.** About 9 km

POSTSCRIPT

More experiments to demonstrate the particle nature of light

P1.1 Blackbody radiation

Any object emits some radiation (visible light, infrared or ultraviolet radiation) and absorbs part of the radiation falling on it. A blackbody is an object that absorbs all the radiation that falls on it. The radiation emitted by a blackbody is called *blackbody radiation*. This radiation is not monochromatic, it contains a distribution of energy in various wavelengths. The distribution of total light energy in different wavelengths, that is, the spectral distribution in a blackbody radiation has a very special form which depends on the temperature of the radiating body. If you have an enclosure and keep it at a fixed temperature, the radiation inside has the same form of energy distribution and hence is the same as blackbody radiation.

Based on classical wave theory describing stationary waves in an enclosure, and classical thermodynamics, Rayleigh derived an equation for the spectral distribution of blackbody radiation. This equation, commonly known as Rayleigh–Jeans law, is

$$u_\lambda = \frac{8\pi}{\lambda^4} kT \tag{P1.1}$$

where $u_\lambda d\lambda$ denotes the energy of radiation per unit volume in the wavelength range λ to $\lambda + d\lambda$, T is the temperature in Kelvin and k is the Boltzmann constant. What does Equation P1.1 mean? Take an enclosure (like a metallic shell) of volume V and keep its temperature fixed at T. Look at the radiation inside, with wavelength only in the range λ to $\lambda + d\lambda$, and find its energy. Divide by the volume and what you get is $u_\lambda d\lambda$. According to Rayleigh-Jeans law this should match with Equation P1.1.

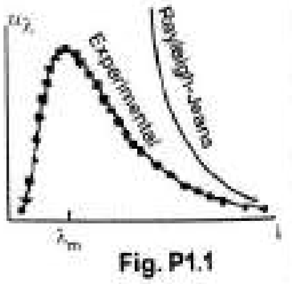


Fig. P1.1

How do the experimental results compare with this equation? Figure P1.1 shows the comparison schematically. For larger wavelengths they compare very well. But for smaller wavelengths, it is all nonsense. Rayleigh–Jeans law predicts rapidly increasing u_λ as one decreases λ, but that is not the actual case. The spectral distribution has a maximum at some wavelength λ_m and decreases on both sides of it. Max Planck made a big advancement in quantum theory when he put forward a model saying that energy of any oscillation can be absorbed or emitted only in units of a basic energy E which is proportional to the frequency of the oscillation. In case of light, this means, the energy of various modes of stationary waves in the enclosure can be ε, 2ε, 3ε,... etc., with $\varepsilon = h\nu = hc/\lambda$, where h is a constant. Using this hypothesis he derived the following equation for spectral distribution

$$u_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}. \tag{P1.2}$$

This equation matches extremely well with experimental results, in the entire range of wavelength, when the value of h is given 6.6×10^{-34} Js. For large wavelengths, Equation P1.2 approaches the Rayleigh–Jeans law explaining why the later was successful at large wavelengths.

Planck's hypothesis was a great revolution and the constant h is rightly called Planck's constant

P1.2 Discrete wavelengths in atomic spectra

All of us are familiar with mercury vapour lamps and sodium vapour lamps used to light our living rooms and streets. Similarly, one can fill a discharge tube with hydrogen and connect the two electrodes in the tube to appropriate voltage source. As the electric current goes through, the hydrogen atoms in the tube emit light. If this light is examined by suitable gratings one finds very specific discrete wavelengths. In the visible region, the first four wavelengths in decreasing order are 656.6 nm, 486.4 nm, 434.3 nm and 410.4 nm. No light is emitted with arbitrary wavelengths like 600 nm or 575 nm etc. These data were known to the scientists in early twentieth century but there was no clue why only some specific wavelengths are present in the atomic spectra.

Niels Bohr in 1913 put forward a wonderful model which is so popular even today. In essence, it assumes that the electron of a hydrogen atom orbits around the nucleus (proton) in a circular path, the radius of which can have certain specific values. For each such circular path, there is a corresponding fixed energy. Light is emitted when the electron jumps from one path of energy E_i to another path having a lower energy E_f. The light emitted in the process has energy $E_i - E_f$. The light is emitted in quanta or lumps of definite energies.

How does one understand the specific values of the wavelength emitted by hydrogen gas? Bohr suggested that the electron can go only in those circular orbits for which the angular momentum of the electron is an integral multiple of $h/2\pi$ where h is the Planck's constant. In other words,

$$m_e \upsilon_n r_n = n\frac{h}{2\pi} = n\hbar \tag{P1.3}$$

where r_n and υ_n are the speeds corresponding to the orbit with angular momentum $n\hbar$.

This equation together with the force equation

$$\frac{e^2}{4\pi \epsilon_\circ r_n^2} = m_e\left(\frac{\upsilon_n^2}{r_n}\right) \tag{P1.4}$$

gives,

$$r_n = \frac{4\pi \epsilon_\circ \hbar^2 n^2}{m_e e^2} \tag{P1.5}$$

and,

$$\upsilon_n = \frac{e^2}{4\pi \epsilon_\circ \hbar n} \tag{P1.6}$$

From these, you can write the energy corresponding to the n^{th} orbit,

$$E_n = -\frac{m_e e^4}{2(4\pi \epsilon_\circ)^2 \hbar^2 n^2}. \tag{P1.7}$$

Thus, when the electron jumps from the n^{th} orbit to the m^{th} orbit, the energy of the photon emitted is

$$E_n - E_m = \frac{m_e e^4}{2(4\pi \epsilon_\circ)^2 \hbar^2}\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \tag{P1.8}$$

The wavelength corresponding to this radiation is

$$\lambda = \frac{hc}{E_n - E_m}. \tag{P1.9}$$

Wavelengths in visible region result when the electron jumps from higher energy orbit to the orbit corresponding to $n = 2$. Thus you put $m = 2$ and $n = 3, 4, 5, \ldots$ in equations (P1.8) and (P1.9) and get the wavelengths of the visible light that can come from hydrogen gas, according to Bohr's model.

When the energies allowed by the model were equated to hc/λ, the wavelengths λ came out to be almost exactly the same as those observed experimentally. Thus it was again a great leap in establishing the particle nature of light. You can count the quanta, for each transition, there is one quantum.

P1.3 Compton effect

Compton reported in 1923 that when X-rays are scattered from materials, the scattered X-rays have larger wavelengths than the incident X-rays. The change in wavelength has an upper limit, meaning by, X-rays of wavelength λ will scatter with a wavelength in the range λ to $\lambda + \Delta\lambda$ where $\Delta\lambda$ has some specific upper limit. This observation could be explained by treating the scattering of X-rays from a material as a collision between a photon of energy hc/λ and an electron of the material which is almost free and assumed to be at rest in the beginning.

Relativistic equations are to be used for linear momentum and energy conservations. Linear momentum of the photon before the collision is h/λ and after the collision it is h/λ' (Figure P1.2). The linear momentum of the electron before the collision is zero and that after the collision is p_e. The photon is scattered through an angle ϕ and the electron is deflected at an angle θ from the line of impact. The equations corresponding to conservation of momentum and energy are

$$\frac{h}{\lambda} = \frac{h}{\lambda'}\cos\phi + p_e\cos\theta$$

$$0 = \frac{h}{\lambda'}\sin\phi - p_e\sin\theta$$

and

$$\frac{hc}{\lambda} + m_0c^2 = \frac{hc}{\lambda'} + \sqrt{m_0^2c^4 + p^2c^2}\,.$$

Solving these equations, one gets

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{mc}(1 - \cos\phi) \tag{P1.10}$$

The maximum value of $\Delta\lambda$ is $\frac{2h}{mc}$ when the x-ray is observed at $\phi = \pi$, that is, when it is scattered in the direction opposite to the incident direction. The quantity $\frac{h}{mc}$ is called *Compton wavelength* of electron.

Such a shift in the wavelength of X-rays or γ-rays when they scatter from a material is shown in many experiments including the detection of γ-rays in a nuclear detector. The values shown up are indeed according to Equation P1.3. All this shows that electromagnetic radiation has particle properties (together with the wave properties) and at the time of interaction with an electron, this particle property shows up. Radiation can be treated as a stream of photons.

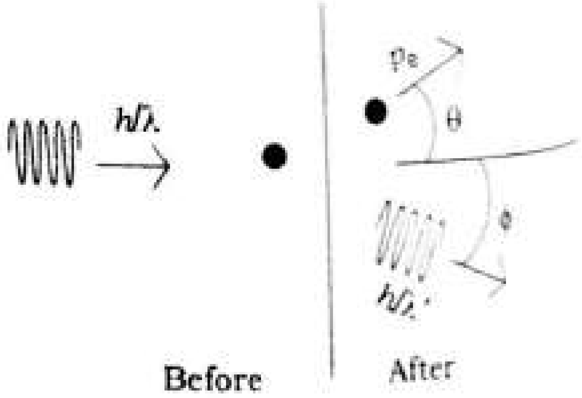


Fig. P1.2

P1.4 Single photon interference experiments

A few decades ago, Young's double-slit interference at a single photon level was only a topic of imagination and discussion. But with the advancement of technology it has become much more common. In several academic institutions this is in regular laboratory course and all students in the course do it. At several places this is used as a demonstration experiment. Two basic requirements for observing interference at single photon level are

(a) an extremely weak source that ensures that at any given instant, there is at most one photon in whole of the apparatus

(b) a very sensitive light detector, which can record light at the level of one photon.

The first requirement is met by using a source of low intensity (say 1mW He-Ne laser) and passing the light through an attenuator that absorbs most of the light. Attenuators are used which reduce the intensity by a factor of 10^{11} or so. At these intensities you will find on the average one photon per 9 km of the beam. This light goes through a pinhole in a darkened chamber which houses the double slit and the detector probe. As the length of the apparatus is hardly a meter, you may rest assured that at no instant you have more than one photon in the apparatus.

The second issue is the detection of light. Now-a-days CCD cameras are available which are several tens of million times more sensitive than the usual video camera we use for photography. A CCD camera has an array of pixels and the video receiver reads the illumination at these pixels frame by frame. The data are stored in a computer for specified time and the image can be displayed. Nice images are given at website of several universities (for example, you can visit Princeton University http://Ophelia.princeton.edu/~page/single_Photon.html). They used three slits for interference and a 1mW He-Ne laser attenuated by a factor of 0.2×10^{11}. As the exposure time is increased interference pattern is built up from individual impacts.

In the demo experiment described at the Harward University website they use two slits and a sliding cover on the slit holder which can close any of the two slits. If two slits are opened, one by one for equal time intervals while the data collection goes on, no interference pattern is observed. But if both slits are opened together, interference pattern is built up from the individual events.

2

Rules of Measurement– Lessons from Polarized Light

2.1 Polarization of light

Going by the wave picture, light is described as oscillating electric and magnetic fields. The electric field $\mathbf{E}$, the magnetic field $\mathbf{B}$ and the direction of propagation are mutually perpendicular for light traveling in vacuum and in many of the transparent media. Once the electric field $\mathbf{E}$ is given, the magnetic field $\mathbf{B}$ can be easily obtained from the relation $\mathbf{B} = \mathbf{k} \times \mathbf{E}/c$ where $\mathbf{k}$ is the unit vector in the direction of propagation. So it is sufficient to give $\mathbf{E}$ to describe a light wave. A monochromatic light beam moving in the x-direction is represented by

$$\mathbf{E} = \mathbf{E}_0 \sin(kx - \omega t). \tag{2.1}$$

The field $\mathbf{E}$ can be in any direction in the y-z plane. If the electric field is always parallel to a fixed direction in space, the light is called *linearly polarized*. For example, the wave equation

$$\mathbf{E} = E_0\, \hat{\mathbf{e}}_2 \sin(kx - \omega t) \tag{2.2}$$

represents a linearly polarized light. Here $\hat{\mathbf{e}}_2$ is the unit vector in the y-direction so that the electric field is always parallel to the y-direction. The light is said to be polarized in the y-direction. Similarly the wave equation

$$\mathbf{E} = E_0\, \hat{\mathbf{e}}_3 \sin(kx - \omega t) \tag{2.3}$$

represents a linearly polarized light, polarized in the z-direction. Here $\hat{\mathbf{e}}_3$ is the unit vector in the z-direction.

An ordinary source of light, such as a sodium vapour lamp, sunlight, a candle, etc., gives unpolarized light. The electric field keeps changing its direction randomly and frequently in the plane perpendicular to the direction of propagation. There are a number of ways to get a linearly polarized light from an unpolarized light. A very simple way to do this is to take a plane mirror made of ordinary glass and send a parallel beam of monochromatic light at an angle of incidence 57^0 (more precisely $\tan^{-1}\mu$, μ being the refractive index of glass). The reflected light will be linearly polarized with electric field perpendicular to the plane of incidence. A device used to polarize light is called a *polarizer*.

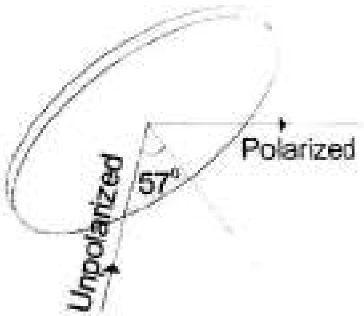


Fig 2.1

2.2 Polarization by a Nichol prism

Nichol prism is a commonly used device to study polarization of light. It is made from a transparent crystal of calcite. The crystal has a shape of a parallelepiped with its length about three times its width. All faces are in the shape of a parallelogram with specific angles between the sides. To make a Nichol prism, the crystal is cut along a particular plane in two parts, the two faces are polished and rejoined by a transparent layer of a particular cement called Canada balsam. The faces are slightly rubbed to change the angles a little. A schematic diagram of a Nichol prism is shown in

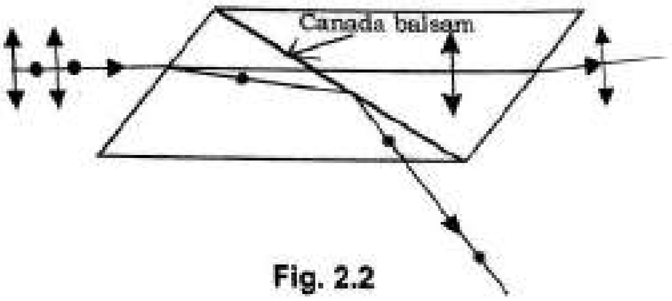
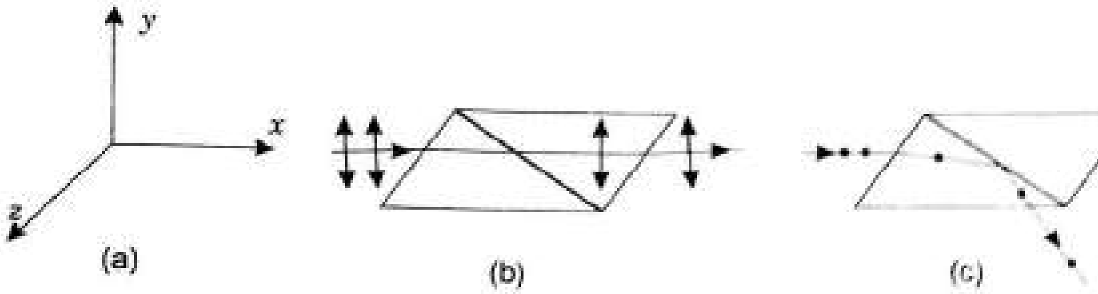


Fig. 2.2

Figure 2.2. When an unpolarized beam falls on its face in a particular direction, a part of it gets reflected at the Canada balsam and the rest of it goes through it. Thus the beam splits in two parts. The one transmitted through the prism is linearly polarized with its electric field in the plane of the diagram and the other reflected at the Canada balsam is linearly polarized with its electric field perpendicular to the plane of the diagram. In Figure 2.2, I show the electric field of the transmitted beam by double arrows in the plane of the diagram and that of the reflected beam by dots, usual notation to indicate a direction perpendicular to the plane of the diagram.

What happens if you send a linearly polarized light to the Nichol prism? Let me first define the coordinate axes. I take x-axis along the direction of the incident beam, y-axis in the plane of the diagram and the z-axis perpendicular to the plane of the diagram as shown in Figure 2.3a. Suppose the incident beam is polarized in the y-direction (Figure 2.3b). The electric field is given by Equation 2.2, that is, $\mathbf{E} = E_0\, \hat{\mathbf{e}}_2 \sin(kx - \omega t)$.



(a) (b) (c)

Fig. 2.3

Let me denote this state of polarization by the symbol $|\mathrm{e}_2\rangle$ (Polarization in the plane of the figure). In this case whole of the light gets transmitted through the prism and no part is reflected. Neglecting a small amount of absorption in the prism, the intensity I_0 of the transmitted beam is the same as that of the incident beam. Also the state of polarization of the transmitted beam is $|\mathrm{e}_2\rangle$ (the direction of the $\mathbf{E}$-field almost the same), that is, the same as that of the incident beam.

Next, suppose the incident light beam is polarized in the z-direction (Figure 2.3c). The electric field is given by Equation 2.3, that is,

$$\mathbf{E} = E_0\, \hat{\mathbf{e}}_3 \sin(kx - \omega t)\,.$$

Let me call this state of polarization as $|\mathrm{e}_3\rangle$ (Polarization perpendicular to the plane of the figure). Whole of the beam gets reflected in this case. The intensity of the reflected beam is I_0 and the state of polarization of this beam is $|\mathrm{e}_3\rangle$, i.e., the same as that of the incident beam.

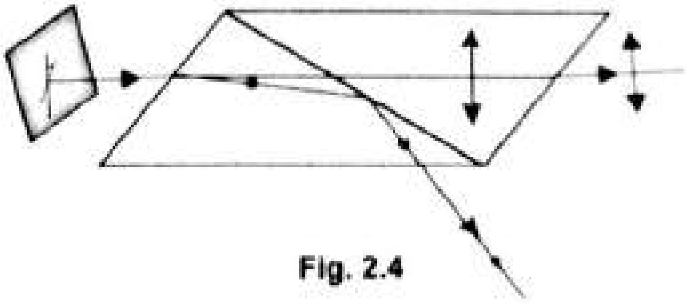
What happens if a linearly polarized light given by

$$\mathbf{E} = E_0(\cos\theta\, \hat{\mathbf{e}}_2 + \sin\theta\, \hat{\mathbf{e}}_3)\, \sin(kx - \omega t) \tag{2.4}$$

falls on the Nichol prism? This is a combination of waves represented by Equations 2.2 and 2.3 with the weights $\cos\theta$ and $\sin\theta$. I can write the state of polarization as

$$|\mathrm{e}\rangle = |\mathrm{e}_2\rangle \cos\theta + |\mathrm{e}_3\rangle \sin\theta\,. \tag{2.5}$$

Note that the electric field is still perpendicular to the direction of propagation. What you find is that a part of the light gets transmitted and a part reflected. The intensity of the transmitted beam is $I_0 \cos^2\theta$ and that of the reflected beam is $I_0 \sin^2\theta$. Also the transmitted light is polarized in the y-direction whereas the reflected



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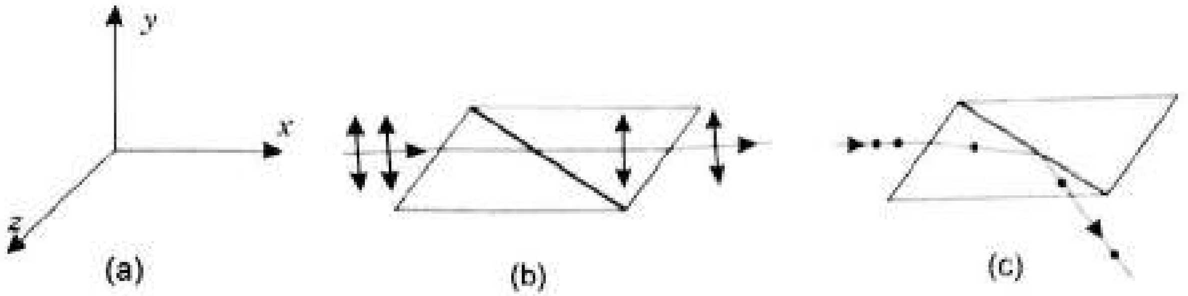

(a) (b) (c)

Fig. 2.3

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$$\mathbf{E} = E_0(\cos\theta\,\hat{\mathbf{e}}_2 + \sin\theta\,\hat{\mathbf{e}}_3)\ \sin(kx - \omega t) \tag{2.4}$$

falls on the Nichol prism? This is a combination of waves represented by Equations 2.2 and 2.3 with the weights $\cos\theta$ and $\sin\theta$. I can write the state of polarization as

$$|e\rangle = |e_2\rangle\cos\theta + |e_3\rangle\sin\theta. \tag{2.5}$$

Note that the electric field is still perpendicular to the direction of propagation. What you find is that a part of the light gets transmitted and a part reflected. The intensity of the transmitted beam is $I_0\cos^2\theta$ and that of the reflected beam is $I_0\sin^2\theta$. Also the transmitted light is polarized in the *y*-direction whereas the reflected

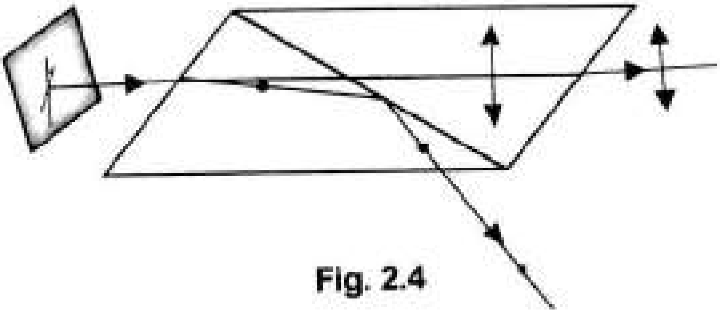

Fig. 2.4

light is polarized in the z-direction. These facts are represented
these observations is very simple.

The wave given by Equation 2.4 is a combination of two waves

$$\mathbf{E} = (E_0 \cos\theta)\,\hat{\mathbf{e}}_2 \sin(kx - \omega t)$$

and
$$\mathbf{E} = (E_0 \sin\theta)\,\hat{\mathbf{e}}_3 \sin(kx - \omega t).$$

The first gets completely transmitted and the other gets completely reflected just as in the case discussed in Figure 2.3. The intensity is proportional to the square of the amplitude; hence th transmitted and reflected beams have intensities $I_0 \cos^2\theta$ and $I_0 \sin^2\theta$ respectively.

2.3 Polarization with a weak source

Let me bring some twist in the story. Suppose you perform the experiment represented in Figu 2.4 but now E_0 is very small. Put light detectors D1 and D2 to receive the transmitted and reflec beams respectively. Assume, for the sake of arguments that when a photon enters a detector, detector beeps. If you do the experiment with a very weak source, you will hear beeps intermitten and not continuously. Occasionally, one of the two detectors will beep and then there will be silen Again there will be a beep. Light does not arrive the detectors continuously. It comes as discrete lu of energy, the photons. Distinct beeps at intervals means that the source is so weak that phot arrive one by one at the Nichol prism. Also you don't hear beeps from the two detect simultaneously. It is either D1 or D2, but not D1 and D2. The photons are not splitting at the Can balsam. A photon either goes to D1 or to D2. All beeps are equally loud again suggesting that phot do not split.

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R_1 : The photon is transmitted

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(b) It is not possible, in general, to predict beforehand which result will be obtained measurement. But the probabilities of different results can be predicted.

(c) If the initial state of polarization is $|e_2\rangle$ or $|e_3\rangle$, the result of the measurement is beforehand. In the former case the result has to be R_1 and in the latter case it is R_2. special states are called *pure states* of this measurement. $|e_2\rangle$ is the pure corresponding to the possible result R_1 and $|e_3\rangle$ is the pure state corresponding possible result R_2.

(d) If the initial state $|e\rangle$ of polarization is not itself a pure state, the result of measure not definite. If $|e\rangle = |e_2\rangle\cos\theta + |e_3\rangle\sin\theta$, the probability of the result R_1 is $\cos^2\theta$ and R_2 is $\sin^2\theta$.

light is polarized in the z direction. These facts are represented in Figure 2.4. The explanation for these observations is very simple.

The wave given by Equation 2.4 is a combination of two waves

$$E = (E_0 \cos\theta)\, e_2 \sin(kz - \omega t)$$

and $$E = (E_0 \sin\theta)\, e_3 \sin(kz - \omega t).$$

The first gets completely transmitted and the other gets completely reflected just as in the cases discussed in Figure 2.3. The intensity is proportional to the square of the amplitude; hence the transmitted and reflected beams have intensities $I_0 \cos^2\theta$ and $I_0 \sin^2\theta$ respectively.

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(d) If the initial state $|e\rangle$ of polarization is not itself a pure state, the result of measurement is not definite. If $|e\rangle = |e_2\rangle\cos\theta + |e_3\rangle\sin\theta$, the probability of the result R_1 is $\cos^2\theta$ and that of R_2 is $\sin^2\theta$.

(e) If the initial state of polarization of the photon is $|e\rangle = |e_2\rangle\cos\theta + |e_3\rangle\sin\theta$ and the measurement gives the result R_1, the state of polarization just after the measurement will be $|e_2\rangle$, whatever be the value of θ. Similarly, if the result of measurement is R_2, the state of polarization just after the measurement will be $|e_3\rangle$. So, the state of polarization just after the measurement is the same as that in the pure state corresponding to the result obtained. Thus a measurement changes the state of polarization from $|e\rangle$ to either $|e_2\rangle$ or $|e_3\rangle$.

Similar rules apply in general to all measurements on quantum systems.

2.4 You learned in this chapter

- There are some fixed possible results R_1, R_2, R_3...... of a measurement on a system.
- Corresponding to each result R_i, there is a pure state $|i\rangle$ of the system.
- If the system just before the measurement happens to be in a pure state $|i\rangle$, the result of measurement is sure to be R_i.
- If the system just before the measurement is not a pure state of the measurement, the result of measurement cannot be predicted with certainty.
- If the state of the system before the measurement is a linear combination of the pure states, such as

  $$|\Phi\rangle = \sum_i c_i |i\rangle, \qquad \left(\sum_i |c_i|^2 = 1\right)$$

  the probability of getting the result R_i is $|c_i|^2$.
- If the result of the measurement is R_i, the state of the system just after the measurement has to be $|i\rangle$, irrespective of what the initial state was. Thus the measurement abruptly changes the state of the system.

EXERCISES

1. A polarizer is kept with its transmission axis parallel to the y-axis (If the polarization of the incident light is along the transmission axis, the light gets completely transmitted). A light beam moving in z-direction and having amplitude of electric field $\mathbf{E} = E_0(5\hat{e}_1 + 12\hat{e}_2)$ falls on the polarizer. Find the probability that (a) a given photon will be transmitted through the polarizer, (b) out of two given photons falling on the polarizer, one is transmitted and the other is blocked, (c) out of two given photons falling on the polarizer, at least one is transmitted. **Ans.** (a) $(12/13)^2$ (b) $2\times(5/13)^2\times(12/13)^2$ (c) $1-(5/13)^4$

2. Two polarizers 1 and 2 are kept one after the other with their transmission axes parallel to the vectors $2\hat{e}_2 + 3\hat{e}_3$ and $3\hat{e}_2 + 2\hat{e}_3$ respectively. A photon of light traveling in x-direction and having polarization (electric field) in the y-direction falls on polarizer 1. Find the probability of its getting transmitted through both the polarizers. **Ans.** 576/2197

3. A measurement on a system has three possible outcomes R_1, R_2 and R_3. The corresponding pure states of the system are $|1\rangle$, $|2\rangle$ and $|3\rangle$ respectively. The system is prepared in the state $|\phi\rangle = c\big[|1\rangle + 2|2\rangle + 3|3\rangle\big]$ and the measurement is made. What is the probability that the result will be R_2? **Ans.** 2/7

4. A particular measurement on a system has two possible outcomes R_1 and R_2. The corresponding pure states are $|1\rangle$ and $|2\rangle$ respectively. The system is prepared in the state $c\big[|1\rangle + \sqrt{3}|2\rangle\big]$ and the measurement is made twice in succession. Find the probability that the results will be (a) R_1 and R_1 (b) R_2 and R_2 (c) R_2 and R_1 (d) R_1 and R_2. **Ans.** (a) 1/4 (b) 3/4 (c) 0 (d) 0

3

Material Particles Also Need Wave Description

3.1 You too electron

There was a big confusion for more than hundred years about the nature of light, whether it is a particle or a wave. But electron, once it was discovered in 1897 by Thompson, was quite noncontroversial. It makes a sharp mark on the screen of a cathode ray tube. Apply an electric and/or a magnetic field and the electron is deflected. Its position on the screen can be calculated using Newton's laws of motion with $\mathbf{F} = q\,(\mathbf{E} + \mathbf{v} \times \mathbf{B})$. It has a definite mass 9.1×10^{-31}kg and a definite charge -1.6×10^{-19}C. People always visualized it as a tiny particle having a definite position, definite momentum and a definite energy at any given time. But it turned out to be not so innocent.

Twenty seven years after the discovery of electron, de Broglie in 1924, still in his twenties, suggested that if light can have dual character (wave as well as particle), material particles like electron should also have it. He proposed that the wavelength λ of the wave associated with a particle is related to the momentum of the particle as

$$\lambda = \frac{h}{p} \tag{3.1}$$

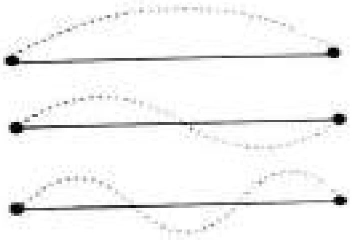


Fig. 3.1

where h is the Planck's constant and p is the momentum of the particle. This is the same relation as established for a photon. We call this relation the *de Broglie relation*. de Broglie did not have much experimental support to justify his hypothesis, but he showed that by assuming a wave picture for electron one can explain the discrete orbits in hydrogen atom. If you have a string of length L, fixed at both ends, standing waves can be produced on it by vibrating it with particular frequencies. These frequencies are obtained by demanding that the two fixed ends should be nodes and hence the length of the string should be an integral multiple of $\lambda/2$. What happens if you have a circular wire of radius r and try to produce a standing wave on it? If a point on the wire is a node, it should remain a node all the time and if a point is antinode, it should remain an antinode all the time. To achieve this the total length of the wire should be an integral multiple of λ. According to de Broglie's suggestion, the wavelength of the electron is h/p where p is its linear momentum. If it orbits in a circle of radius r, the length available for this wave is $2\pi r$. To have a stationary pattern, this length should be an integral multiple of the wavelength λ. Thus,

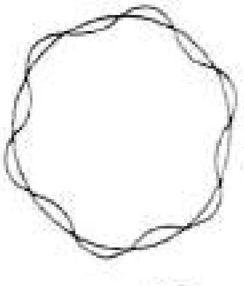


Fig. 3.2

$$2\pi r = n\frac{h}{p}$$

or

$$rp = n\frac{h}{2\pi}$$

or

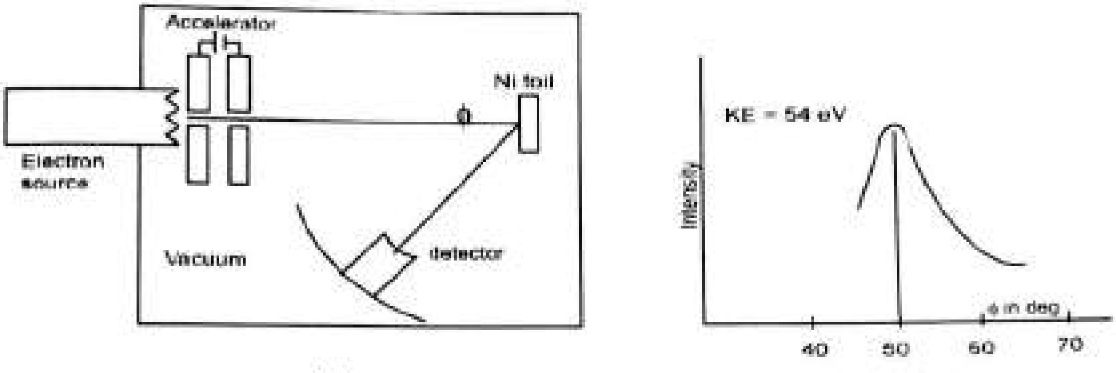
$$l = n\frac{h}{2\pi}$$

where l is the angular momentum of the electron in the orbit. This gives justification to the Bohr's model having discrete orbits.

The experimental confirmation for de Broglie hypothesis came in 1927 when Davisson and Germer found that electrons were diffracted by materials much like X-rays. Let me describe this experiment in somewhat more details.

3.2 Davisson and Germer Experiment

Clinton Davisson and Lester Germer were doing experiments on angular distribution of electrons scattered from a nickel foil. The experimental arrangement can be schematically shown as in Figure 3.3a. They had no intention of testing de Broglie hypothesis of wave character of material particles. But Brahmaji had already written Nobel prize for them. Due to some problem, air leaked into the evacuated chamber oxidizing the nickel foil. The foil was given a special heat treatment to expel the oxygen and the experiment was resumed with the heat-treated foil. And now the results were quite different. The electrons scattered intensely at a specific angle ϕ which depended on the initial kinetic energy. For example, when the initial kinetic energy of the electron was 54 eV, the intensity of the scattered electrons increased sharply at $\phi = 50^0$. Figure 3.3b shows schematically the variation of the intensity of the scattered beam with the angle ϕ. Such a variation of intensity with angle was known for X-ray diffraction and Davisson and Germer soon knew that they were observing the wave character of electrons as proposed by de Broglie.



(a) (b)

Fig. 3.3

Why did the result change so drastically when the nickel foil was heat treated? It got well crystallized due to the heat treatment. The atoms got arranged in regular patterns. Such an ordered arrangement of atoms reflect the X-rays in very specific directions. This is a common phenomenon and this fact is used to determine the crystal structure using X-rays. Let me describe why X-rays are reflected only in specific directions and how these directions are related to the crystal structure.

Suppose, X-rays are sent to the crystal making an angle θ with the planes of atoms as shown in Figure 3.4. A part of the X-ray waves is diffracted from the top plane of atoms, another part from the next plane, and so on. The difference in path length travelled by the waves diffracted from consecutive planes is $2d\sin\theta$ as can be seen from the geometry of Figure 3.4. Here d is the distance between the consecutive planes of the atoms. The diffracted wave has a large intensity for directions satisfying

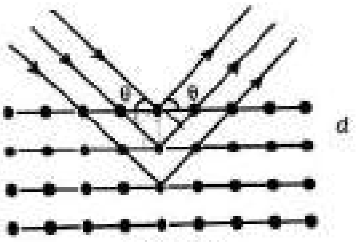


Fig. 3.4

$$2d\sin\theta = \lambda \qquad (3.2)$$

where λ is the wavelength of the X-rays.

There is an interesting fact about the planes of atoms in a crystal. The planes in Figure 3.4 were drawn mentally. The crystal has atoms arranged in a regular pattern but planes are our own imagination. We can imagine planes through the same atoms in other ways also, for example, as shown in Figure 3.5. The arrangement of atoms is the same as in Figure 3.4 but the planes are drawn differently. The separation between consecutive planes, d, is also different in this case. Thus, for the same crystal, we have several values of d and hence several values of θ are possible. At each of these values of θ, the X-ray intensity will show a peak. Intensities of the peaks are different for different θ and often the peak corresponding to a particular θ is quite strong as compared to others.

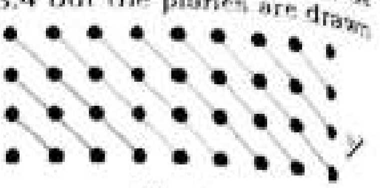


Fig. 3.5

In the experiment of Davisson and Germer, the wave associated with the electrons was diffracted from the planes of atoms in the same way. The electron beam having electrons of 54 eV kinetic energy was incident normally on the surface of the nickel foil and was scattered strongly at $\phi = 50°$ with the normal to the surface (Figure 3.6). Thus the planes of atoms responsible for this scattering make an angle 65° [i.e., (180°–50°)/2] with the incident beam or 25° with the surface of the foil. The separation between consecutive planes in this family was known from X-ray diffraction to be equal to 0.0909 nm. The wavelength of the electron waves may be calculated using the same equation as applied in X-ray diffraction. So,

$$\begin{aligned}\lambda &= 2d\sin\theta \\ &= 2 \times (0.0909\ \text{nm}) \times \sin 65^\circ \\ &= 0.165\ \text{nm}.\end{aligned}$$

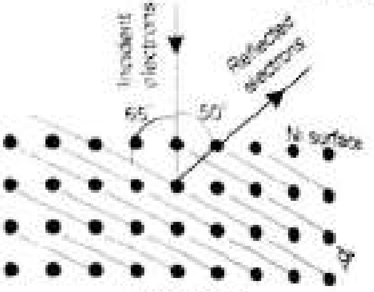


Fig. 3.6

This is the wavelength of the waves associated with the electrons as obtained from the experiment. Using de Broglie hypothesis the wavelength for an electron having kinetic energy of 54 eV should be,

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mK}} = \frac{hc}{\sqrt{2mc^2K}}\,.$$

$$= \frac{1240\ \text{eV nm}}{\sqrt{2 \times (511\ \text{keV})(54\ ev)}} = 0.166\ \text{nm}\,.$$

The result from Davisson–Germer experiment agrees extremely well with the hypothesis put forward by de Broglie.

I had been using the term scattering of electrons in describing the Davisson–Germer experiment. More appropriate term is diffraction of electrons as the physics at work is diffraction of the wave associated with the electrons.

Electron diffraction has become a common tool to probe internal structure of materials at micron and nanometer levels. Images with magnification of the order of 100,000 are quite common with Transmission Electron Microscopy which is based on electron diffraction.

3.3 Double-slit experiment with electrons

If electrons have wave characteristics one should be able to do Young's double-slit experiment with electrons. Yes, it is possible to do such an experiment and it has been done. Electrons with a particular kinetic energy are sent on a double-slit and those coming out on the other side are counted by putting appropriate detectors. Electrons arrive at certain positions of the detector in a large number showing constructive interference of waves and very few electrons reach at certain other positions showing destructive interference. It also verifies the de Broglie relation $\lambda = h/p$.

Imagine you do the double-slit experiment with a very weak source of electrons so that electrons fall on the double-slit one by one. This rules out any possibility of electrons colliding among themselves preventing them from reaching certain places. The data can be stored in a computer so that you have a permanent record of the electron impacts. If the experiment is performed for a very short time you only get some random impacts here and there. But as you prolong the duration of the experiment, these impacts start showing up interference pattern. It is clear that even when a single electron goes through the double-slit, wave interference takes place. Where the electron will be detected is decided by the intensity of the wave associated with it. The wave corresponding to this single electron passes through both the slits simultaneously and hence interferes according to the usual wave mechanics. The wave intensity decides the fate of the electron.

I do not intend to give an impression that an electron and the wave associated with it are two different physical entities and have separate existence. In order to describe the observed behaviour of an electron, a wave aspect is necessary. The electron itself behaves as a wave and also as a particle.

3.4 The Trishul like symbol ψ—wave function

In Chapter-1, I told you that a photon has both particle-like and wave-like characters. In this chapter I told you that an electron too has a particle-like as well as a wave-like character. In both cases the object (photon or electron) is always detected as a particle, it interacts with other materials as a particle, but the probability of its being found at a place is governed by the wave that always accompanies the object. The situation with electron is different from that with photon in one aspect which will make the mathematician in you feel happy. The wave associated with a photon, as described so far in this book is electromagnetic wave. The wave is described in terms of electric field and magnetic field which one can visualize, which exert force on a particle and so on. But the wave quantity associated with an electron or a material particle is very abstract and does not correspond to any measurable physical quantity. Often it involves complex numbers (involving square root of negative numbers).

The most popular symbol to represent the wave quantity associated with a material particle is $\psi(\mathbf{r}, t)$ and we call it the *wave function* of the particle.

So when we consider a material particle like electron, we say that there is a wave function $\psi(\mathbf{r}, t)$ associated with it. And this wave function is said to represent the "state" of the particle. At a given location $\mathbf{r}$ and at a time t, there is a definite value of this wave function which may be complex. At a given location $\mathbf{r}$, the value changes with time and at a given time its value is different at different positions. The connection between the wave function and the probability of finding the electron there, is given by what is called *Born's interpretation* of wave function. Let me now describe it.

Consider a point with position vector $\mathbf{r}$. Construct a small volume $d\tau$ around this point (Figure 3.7). The probability of finding the particle in this volume at time t is given by

$$dP = c\psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t)\,d\tau = c|\psi(\mathbf{r}, t)|^2\,d\tau \tag{3.3}$$

where $\psi^*(\mathbf{r}, t)$ is the complex conjugate of $\psi(\mathbf{r}, t)$ and c is a constant. The probability of finding the particle somewhere in the entire space must be 1. This means $\int c|\psi(\mathbf{r}, t)|^2\,d\tau = 1$. One can multiply the wave function $\psi(\mathbf{r}, t)$ by an appropriate constant to make

$$\int |\psi(\mathbf{r}, t)|^2\,d\tau = 1\,.$$

The wave function in such a case is called *normalized*. For such a wave function, we can put $c = 1$ in Equation 3.3, so that

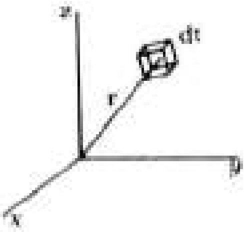


Fig. 3.7

$$dP = |\psi(\mathbf{r}, t)|^2\,d\tau\,. \tag{3.4}$$

The quantity $dP/d\tau = |\psi(\mathbf{r}, t)|^2$ is called the ***probability density function***.

The multiplication of $\psi(\mathbf{r}, t)$ by a constant c does not change the form of the function. It turns out that the state of the particle is related to the form of the wave function $\psi(\mathbf{r}, t)$ and not its value. Thus $\psi(\mathbf{r}, t)$ and $c\psi(\mathbf{r}, t)$ represent the same state of the particle. It is convenient to choose the constant c

such that the wave function is normalized and we can use Equation 3.4 instead of Equation 3.3 for probability.

By now you must have realized that electrons need a totally different description from what the particle dynamics of Newton offers. The new mechanics developed for such systems is called *Quantum Mechanics*, and in this book I intend to tell you the basics of it. The systems which need quantum mechanics for their description can be called quantum systems. I have to tell you many new things about a quantum system which will need your serious attention. So I want to keep the mathematical complications as low as possible. To begin with, I will make a simplification which is not very realistic but it will help you in understanding the new ideas faster. I will assume that our space is one-dimensional and all phenomena have to occur only on the x-axis. The wave function of the particle is then written as $\psi(x, t)$ and the probability of finding the particle in the range x to $x + dx$ is $|\psi(x, t)|^2\, dx$. The probability density is $|\psi(x, t)|^2$.

3.5 State of a particle

You might have been told by your physics teacher that the main task of particle dynamics is to find the position and velocity of the particle at all times if it is known at some initial instant. Given the forces, the equations of dynamics can be solved to get this information. Once the position and velocity of the particle is given, we believe that we know everything about the particle (dynamical aspects) at that time. In other words, the "state" of the particle at a given instant is described by two quantities, position and velocity, at that time.

The dictionary meaning of the word state is something like the condition of the system. You use the phrases "liquid state", "solid state", "stretched state", "compressed state", "crystalline state" etc. Each one of these is used to give the condition of the object in one particular aspect. In quantum mechanics when I say "state", I mean all the aspects together, whatever information one can have for the system, should be contained in the description of the state. If I say that I know the state of the system at an instant, that means I know everything about the system at that instant that it is possible to know.

For quantum system of a single particle, the information about the position at time t is contained in its wave function $\psi(x, t)$. At a given time t, there may not be a definite position of the particle as the particle may be found at various positions with probabilities proportional to $|\psi(x, t)|^2$. But to know anything about its position at a time t (the probabilities for different positions), I must know its wave function $\psi(x, t)$ at time t. Interestingly, if the wave function $\psi(x, t)$ is known at time t, we also get information about the linear momentum of the particle at that instant. And there is further bonus. Not only position and momentum, but also information about all other dynamical quantities can be obtained from the same wave function. Thus the state of a particle at a given instant t, in quantum mechanics, is given by its wave function $\psi(x, t)$ at that time. In fact particles have a property called spin that has no classical analogue and which is not covered by the wave function $\psi(x, t)$ or $\psi(\mathbf{r}, t)$. I will discuss it in details in a later chapter. Till then I will assume that the particles under consideration have no spin or we are discussing only those properties which do not depend on spin.

Since I am talking of a given instant of time, the wave function is a function of x only. To describe the state of the particle at this instant, you have to specify this function of x, i.e., values at all the points, $-\infty < x < \infty$. My first attempt will be to let you know how and what information can be obtained about the particle if the wave function is known at an instant. I will take this instant as $t = 0$ and write the wave function as $\psi(x)$. The question of how the wave function changes with time will be deferred to a later chapter.

Often we use the phrase "the particle in the state $\psi(x)$". It means that at the given time the wave associated with the particle is described by the wave function $\psi(x)$.

The wave function for realistic situations should satisfy the following conditions.

(a) $\psi(x)$ should be finite everywhere. This ensures that the probability of finding the particle in a given range is finite.

(b) $\psi(x)$ should be square integrable. This means, $\int_{-\infty}^{\infty} |\psi(x)|^2 dx$ is finite. This ensures that you can normalize the wave function, making this integral 1. The probability of finding the particle somewhere in the whole space should be 1.

(c) $\psi(x)$ should be continuous everywhere.

These conditions must be satisfied because $|\psi(x)|^2$ represents the probability density.

3.6 The abstract state and the wave function

If you like thinking in terms of abstract quantities, the state of a particle in quantum mechanics is one quantity which you will enjoy. The wave function $\psi(x)$ is only one way to represent the state. This particular representation is called position representation. There are other ways too to represent this state. And it is not necessary to have a representation of the state at all and you can keep working with the abstract notion of the state. P.A.M. Dirac who contributed a lot in the formulation and development of quantum mechanics, introduced the ket symbol $|\ \rangle$ for the abstract state. An identifying symbol is written inside the ket symbol, such as $|\psi\rangle$, to denote a particular state. This symbol will be read as ket psi.

It is like NIRAKAR BRAHM and SAKAR BRAHM. Those who practice advance spiritualism say that God is abstract and has no shape. But for a common man it is easier to work with various representations of God such as Vishnu or Shankar or Hanuman or Saraswati.

In this book, most of the time I will work with explicit representation of a state in terms of wave functions such as $\psi(x)$ or $\psi(\mathbf{r})$. I will still use the ket symbol like $|\psi\rangle$ almost interchangeably with the wave function $\psi(x)$. But in situations where the wave function representation is not adequate, $|\psi\rangle$ will mean the abstract state. Thus if I write $|\psi\rangle = Ae^{ikx}$, this is not an equality in the true sense of mathematics. The left side is an abstract state and the right side is its position representation. By this equation I only mean that I am referring to that particular state.

3.7 An unrealistic but important wave function—Dirac delta function

Imagine a situation where the position of a particle at $t = 0$ is known to be $x = x_0$ with a mathematically precise meaning. The particle is at a 'point', point as defined in geometry, having zero length, zero breadth and zero height but a definite location. You know such a situation is not realistic. Any experiment on position measurement gives a range, however small, $x \pm \Delta x$ as the result. But let us assume there is an *ideal position measurement experiment*, which gives a precise value of the position with zero uncertainty. This is an imaginary experiment. A proton, an electron, a hydrogen atom, or any other particle always has some 'size' as measured in an experiment. But just imagine that the particle under consideration at $t = 0$ is known to be at a single point $x = x_0$ The wave function of the particle in such a state should be zero everywhere except at $x = x_0$. Also the probability density dP/dx should be infinity at $x = x_0$ because $dP = 1$, whereas $dx = 0$. Such a wave function can be written as

$$\psi(x) = A\,\delta(x - x_0)$$

where $\delta(x - x_0)$ is the *Dirac delta function* centered at x_0. Dirac delta function is also called in short *delta function*. Before I move ahead with further discussions on quantum mechanics, let me talk a little more about Dirac delta function to make you more familiar with this function.

3.7.1 Dirac delta function

The value of Dirac delta function $\delta(x - x_0)$ is infinity at $x = x_0$ and zero everywhere else. It looks like an infinitely high spike at $x = x_0$ as partially suggested in Figure 3.8.

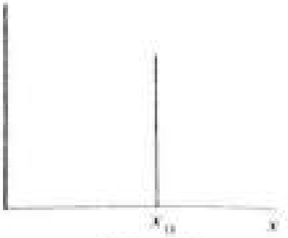


Fig. 3.8

$$\left.\begin{aligned}\delta(x - x_0) &= 0 \quad \text{if } x \neq x_0\\ &= \infty \quad \text{if } x = x_0\end{aligned}\right\} \tag{3.5}$$

But this is not the complete description of delta function. You know, infinity is not a fixed number. The non-ending series 1 + 2 + 3 + 4 + ... adds to infinity and $1^2 + 2^2 + 3^2 + 4^2 + \ldots$ also adds to infinity. But you can compare term by term, the two series are not identical. The Dirac delta function $\delta(x - x_0)$ becomes infinity at $x = x_0$ in such a way that

$$\int_{-\infty}^{\infty} \delta(x - x_0)\, dx = 1. \tag{3.6}$$

In other words, the area under the delta function curve should be 1. Equations 3.5 and 3.6 together make the definition of delta function. Obviously, the contribution to the integration in Equation 3.6 comes only from $x = x_0$ as for all other values of x, the function is zero. So the delta function can also be defined as

$$\begin{aligned}\int_{x_1}^{x_2} \delta(x - x_0)\, dx &= 1 \quad \text{if } x_0 \text{ is included in the range of integration, i.e., } x_1 < x_0 < x_2\\ &= 0 \quad \text{if } x_0 \text{ is not included in the range of integration.}\end{aligned}$$

Delta function may be visualized as a limit of a more familiar function. Think of a rectangular function

$$\begin{aligned}f(x) &= 0 \quad \text{for } x \le x_0 - \frac{a}{2}\\ &= \frac{1}{a} \quad \text{for } x_0 - \frac{a}{2} < x < x_0 + \frac{a}{2}\\ &= 0 \quad \text{for } x \ge x_0 + \frac{a}{2}.\end{aligned}$$

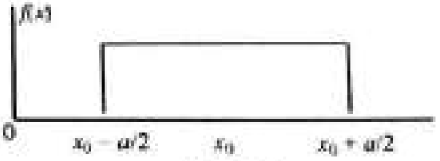


Fig. 3.9

It is plotted in Figure 3.9. The area under the curve is 1 for all values of a. What will happen to this function as $a \to 0$? Its width shrinks to zero and its height becomes infinity. The area under the curve still remains 1. Thus this rectangular function becomes Dirac delta function in the limit $a \to 0$.

Another important representation of delta function is

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx}\, dk. \tag{3.7}$$

An important result, that I will use frequently, is the following. Consider the integration $\int_{-\infty}^{\infty} f(x)\, \delta(x - x_0)\, dx$ where $f(x)$ is any function of x, continuous at $x = x_0$. Contribution to this integral comes only from $x = x_0$ because for all other values of x the integrant is zero. We can write

$$\int_{-\infty}^{\infty} f(x)\, \delta(x - x_0)\, dx = \int_{x_0 - \varepsilon}^{x_0 + \varepsilon} f(x)\, \delta(x - x_0)\, dx$$

where ε is any quantity however small. Taking ε infinitesimally small, we can assume that $f(x)$ is constant at the value $f(x_0)$ in this range $x_0 - \varepsilon$ to $x_0 + \varepsilon$. Then the integration is

$$\int_{x_0-\varepsilon}^{x_0+\varepsilon} f(x_0)\,\delta(x-x_0)\,dx = f(x_0)\int_{x_0-\varepsilon}^{x_0+\varepsilon} \delta(x-x_0)\,dx = f(x_0).$$

So,
$$\int_{-\infty}^{\infty} f(x)\,\delta(x-x_0)\,dx = f(x_0). \tag{3.8}$$

Let me come back to the quantum mechanical description of a particle having wave function $\psi(x) = A\,\delta(x-x_0)$. I remind you, this does not correspond to a realistic situation as a particle can never be found to occupy just a point (zero dimension) in space. The function $\delta(x-x_0)$ does not satisfy any of the three conditions laid down for valid wave functions at the end of Section 3.5. The first condition was that a valid wave function should be finite everywhere. But delta function becomes infinity at one point. The second condition was that $\psi(x)$ should be square integrable. Dirac delta function is not square integrable. It turns out that

$$\int_{-\infty}^{\infty} (\delta(x-x_0))^2\,dx = \infty.$$

The third condition was that the wave function should be continuous. But delta function $\delta(x-x_0)$ jumps suddenly from zero to infinity at $x = x_0$.

All this tells that we cannot have a state of a particle in which its position is precisely known. Delta function is not a realistic wave function. But these delta functions do form a very useful basis to discuss more realistic wave functions.

Before I end the discussion on mathematical properties of Dirac delta function, I would like you to check the dimensions of this function. From Equation 3.6 we see that $\delta(x-x_0)$ has dimensions of (length)$^{-1}$. As $|\psi(x)|^2\,dx$ represents a probability it is a dimensionless number. So the wave function $\psi(x)$ should have dimensions of (length)$^{-1/2}$. If you wish to write a wave function representing a particle in definite position state, you should write it as

$$\psi(x) = A\,\delta(x-x_0)$$

where A has dimensions of (length)$^{1/2}$.

3.7.2 But where is the wave?

I started the discussion of wave properties of particles by showing diffraction of electrons by a crystal and so on. Then I said the wave associated with a material particle is represented by a function $\psi(x)$. And then I talked of a wave function $\psi(x) = A\,\delta(x-x_0)$. Don't you wonder what is wave-like in this function? You are familiar with waves on a string, sound waves in air, electromagnetic waves in space, etc. The wave in all these cases at a given instant $t = 0$ is something like

$$\Phi(x) = \Phi_0 \sin(kx).$$

The mental picture that all of us have for a wave, is something that repeatedly changes from a maximum to a minimum and back to the maximum at regular length intervals as one looks at the different parts of the region at a given time. This length interval is called the wavelength. A wave represented by $\sin(kx)$ has wavelength $\lambda = 2\pi/k$. As x changes by $2\pi/k$, the value of $\sin(kx)$ repeats. What is repeating in the wave function like $A\delta(x-x_0)$ which is just a high spike at $x = x_0$? And what is the wavelength if I insist to call it a wave? I will address this equation in a later chapter.

3.7.3 Delta function as a pure state of ideal position measurement

The state of a particle for which the position is $x = x_0$, is represented by the wave function $\psi(x) = A\,\delta(x - x_0)$. I will call $\delta(x - x_0)$ as basis position eigenfunction corresponding to $x = x_0$ and will denote it by the ket symbol $|x_0\rangle$

If a particle is in the state given by $|x_0\rangle$, it means its wave function at that instant is $A\,\delta(x - x_0)$ and it is at $x = x_0$ and nowhere else. This means, if I do an ideal position measurement (ideal in the sense that it is capable of measuring the position with zero uncertainty), I am sure to get the result $x = x_0$. Recall what you learnt about measurement in Chapter-2. For each measurement, there are certain possible results and with each result there is associated a state called a pure state. If the state of the particle before the measurement is one of the pure states of that measurement, the measurement is sure to give the corresponding result. Thus $|x_0\rangle$ is a pure state of position measurement, corresponding to $x = x_0$. All values of x from $-\infty$ to $+\infty$ are possible results and with each value x_0 of x there is a pure state $|x_0\rangle$.

3.8 Another unrealistic but important wave function—plane waves

Dirac delta function represents the state of a particle for which position is precisely known $(x = x_0)$ at time $t = 0$. Now I consider the state of the particle in which its linear momentum is precisely known, say $p = p_0$, at time $t = 0$. If p_0 is positive, the particle is moving in the positive x-direction and if it is negative, the particle is moving in the negative x-direction.

Once again, any realistic measurement of linear momentum gives the value of momentum with some uncertainty. The result could be a range $p_0 \pm \Delta p$. But we imagine an *ideal momentum measurement* which gives precisely one value of the momentum with zero uncertainty. Let us see what would be the wave function of a particle whose linear momentum is precisely known to be p_0.

You know how do we define de Broglie wavelength. If a particle has momentum p_0, the wavelength of the associated wave is $\lambda = h/p_0$. If p_0 has a precise value, λ also has a precise value. So the wave is strictly monochromatic (single wavelength). The wave function must have a perfect periodicity, it must repeat its value after every λ on the x-axis in the entire range $-\infty < x < \infty$. The wave function in such a case turns out to be

$$\psi(x) = A\,e^{\frac{i}{\hbar}p_0 x}. \tag{3.9}$$

I immediately face a difficulty in using Equation 3.9. As it contains the imaginary number $i = \sqrt{-1}$. I cannot plot this function. You have to live with it. Graphical assistance is limited in dealing wit wave functions. Can I not use $A\cos\left(\frac{p_0}{\hbar}x\right)$ to represent the wave function of the particle wit momentum p_0? This also has a perfect periodicity. I give you one reason why this choice is no suitable. If $A\cos\left(\frac{p_0}{\hbar}x\right)$ represents the wave function of the particle with momentum p_0, wha would be the wave function for the state with linear momentum $-p_0$? It would be

$$A\cos\left(-\frac{p_0}{\hbar}x\right) = A\cos\left(\frac{p_0}{\hbar}x\right).$$

Thus the wave function for the state with momentum p_0 and $-p_0$ will be the same, which is wron Different states of the particle must correspond to different wave functions. The wave functio

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Dirac delta function represents the state of a particle for which position is precisely known ($x = x_0$) at time $t = 0$. Now I consider the state of the particle in which its linear momentum is precisely known, say $p = p_0$, at time $t = 0$. If p_0 is positive, the particle is moving in the positive x-direction and if it is negative, the particle is moving in the negative x-direction.

Once again, any realistic measurement of linear momentum gives the value of momentum with some uncertainty. The result could be a range $p_0 \pm \Delta p$. But we imagine an *ideal momentum measurement* which gives precisely one value of the momentum with zero uncertainty. Let us see what would be the wave function of a particle whose linear momentum is precisely known to be p_0.

You know how do we define de Broglie wavelength. If a particle has momentum p_0, the wavelength of the associated wave is $\lambda = h/p_0$. If p_0 has a precise value, λ also has a precise value. So the wave is strictly monochromatic (single wavelength). The wave function must have a perfect periodicity, it must repeat its value after every λ on the x-axis in the entire range $-\infty < x < \infty$. The wave function in such a case turns out to be

$$\psi(x) = A\,e^{\frac{i}{\hbar}p_0 x}. \tag{3.9}$$

I immediately face a difficulty in using Equation 3.9. As it contains the imaginary number $i = \sqrt{-1}$, I cannot plot this function. You have to live with it. Graphical assistance is limited in dealing with wave functions. Can I not use $A\cos\left(\frac{p_0}{\hbar}x\right)$ to represent the wave function of the particle with momentum p_0? This also has a perfect periodicity. I give you one reason why this choice is not suitable. If $A\cos\left(\frac{p_0}{\hbar}x\right)$ represents the wave function of the particle with momentum p_0, what would be the wave function for the state with linear momentum $-p_0$? It would be

$$A\cos\left(-\frac{p_0}{\hbar}x\right) = A\cos\left(\frac{p_0}{\hbar}x\right).$$

Thus the wave function for the state with momentum p_0 and $-p_0$ will be the same, which is wrong. Different states of the particle must correspond to different wave functions. The wave function described in Equation 3.9 does not have this difficulty. $\psi(x) = A\, e^{\frac{i}{\hbar}p_0 x}$ represents the particle with momentum p_0 (moving in positive x-direction if p_0 is positive) and $\psi(x) = A\, e^{-\frac{i}{\hbar}p_0 x}$ represents the particle with momentum $-p_0$ (moving in negative x-direction if p_0 is positive). Equation 3.9 itself gives the direction of linear momentum. If p_0 is positive, the wave is moving in positive x-direction and if it is negative, the wave is moving in negative x-direction.

A wave represented by the function e^{ikx} is called a plane wave (at $t = 0$). The full wave function is formed by replacing kx with $(kx - \omega t)$ but I am presently concentrating on the wave function at $t = 0$.

I define the basis momentum eigenfunction corresponding to $p = p_0$ as

$$\psi_{p_0} = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}p_0 x} \tag{3.10}$$

and denote it by the ket symbol $|p_0\rangle$.

Remember, a plane wave is also not a realistic wave function. Though it is finite everywhere and continuous, it is not square integrable. The probability density is

$$|\psi(x)|^2 = \left(A\, e^{\frac{i}{\hbar}p_0 x}\right)^* \left(A\, e^{\frac{i}{\hbar}p_0 x}\right) = A^* A = |A|^2$$

and hence $\int_{-\infty}^{\infty} |\psi(x)|^2\, dx = \infty$. Also the probability density $|\psi(x)|^2$ is the same for all x, $-\infty < x < \infty$. This means the particle can be found in the whole of the space with equal probability at $t = 0$. This is quite unrealistic. If I produce a particle in Srinagar, I cannot expect to find it in Madurai with equal probability.

The momentum of a particle in the state $|p_0\rangle$ is definite, and is p_0. That means if I make an ideal momentum measurement, the result is sure to be p_0. Thus $|p_0\rangle$ is a pure state of the momentum measurement corresponding to the result $p = p_0$. All values $-\infty < p < \infty$ are possible results of measurement and with each such result there is a corresponding pure state, i.e. a plane wave with the proper value of p.

3.9 Wave packet—a more realistic wave function

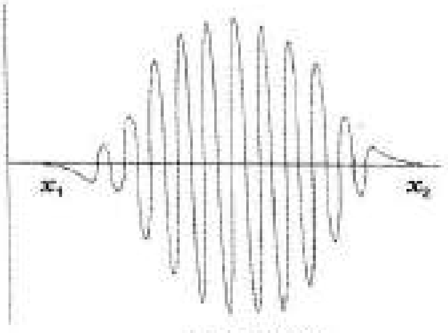


Fig. 3.10

The two cases discussed in Sections 3.7 and 3.8, i.e., the states, $|x_0\rangle$ and $|p_0\rangle$ are unrealistic. The delta function type wave function represents the state where the position is most precisely known, with zero uncertainty, at a particular "point" on the x-axis. On the other hand, the plane wave type wave function represents the state in which the particle is equally likely to be found at all points from minus infinity to plus infinity. Both of these are unrealistic situations. In practice, a particle is known to be confined in a finite range. An electron that is emitted in the picture tube of a television set is known to be confined inside the set. A hydrogen atom in a gas enclosed in a tube is confined in the tube. A particle that is confined to a range $x_1 < x < x_2$ (in our one-dimensional space) should be described by a wave function $\psi(x)$ which is appreciable only in the range $x_1 < x < x_2$ and zero or very small outside this range. Such a wave function is called a wave packet. Figure 3.10 gives a diagrammatic representation of such a wave packet.

3.10 Relativistic and nonrelativistic cases

In classical mechanics you have studied various equations like $K = m_0 v^2/2$, $p = m_0 v$, etc., which involve mass m_0 of the particle. The relation between the kinetic energy K and the linear momentum p is $K = p^2/2m_0$. For particles having speed close to the speed of light in vacuum, you have to use a different set of equations called relativistic equations. Defining $m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$ and $E = mc^2$, some of these equations are,

$$K = mc^2 - m_0c^2$$
$$p = mv$$
$$E^2 = p^2c^2 + m_0^2c^4.$$

m_0 is called the rest mass of the particle as mentioned in the books (for electron it is 9.1×10^{-31} kg) and E turns out to be the total energy. The quantity m_0c^2 is called the *rest mass energy*. You can work out to check that if $v \ll c$, these equations reduce to familiar nonrelativistic equations. When do I use nonrelativistic equations and when does it become necessary to use relativistic equations? That depends on the accuracy level demanded. A quick test for whether one should use relativistic or nonrelativistic equation in a given case is as follows. If the kinetic energy K is much smaller than the rest mass energy m_0c^2 you can use nonrelativistic equations. If K is comparable to m_0c^2 you should use relativistic equations. If K is much larger than m_0c^2, so that the rest mass energy can be neglected, the particle behaves more like a photon. The relation between the total energy (which is almost the same as the kinetic energy) and the linear momentum is then $E \approx pc$.

Remember, the rest mass energy of an electron is 511 keV and that of a proton is 938 MeV to a good approximation.

3.11 You learned in this chapter

- Material particles like electrons, protons, neutrons, molecules, etc., also need wave picture for their description.
- The *state* of a particle (one-dimensional case only) at time t is described by a wave function $\psi(x, t)$. For a given t it is only a function of x and is written as $\psi(x)$.
- The probability of finding the particle in the range x to $x + dx$ in a position measurement is $|\psi(x)|^2\, dx$.
- If the particle is known to be at the point $x = x_0$, its wave function is proportional to $\delta(x - x_0)$.
- If the particle is known to have linear momentum p_0, its wave function is proportional to $\frac{1}{\sqrt{2\pi\hbar}}\; e^{\frac{i}{\hbar}p_0 x}$
- In general, the wave function of a particle at a given time is in the form of a wave packet.

Solved Problems

1. When an electron is accelerated through a potential difference V, its de Broglie wavelength is given by $\lambda = \alpha/\sqrt{V}$ for nonrelativistic speeds. If λ and V represent numerical values in angstrom and volt, find the numerical value of α.

Solution: As an electron is accelerated through a potential difference V, its potential energy is decreased by eV. The kinetic energy gained is equal to this value. So,

$$eV = mv^2/2 = p^2/(2m)$$

or,

$$p = \sqrt{2meV}.$$

de Broglie wavelength is $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}} = \sqrt{\frac{h^2}{2m}\frac{1}{eV}}$.

For an electron, $\frac{h^2}{2m} = 1.5 \text{ eV nm}^2$. So, $\lambda = \sqrt{\frac{1.5 \text{ eV nm}^2}{eV}}$.

If V is put in volts, the energy eV is the same as V electronvolts. Canceling the unit eV from the numerator and the denominator,

$$\lambda = \frac{\sqrt{1.5}}{\sqrt{V}} \text{ nm} \approx \frac{12.25}{\sqrt{V}} \text{ Å}.$$

So,

$$\alpha = 12.25.$$

2. What should be the velocity of an electron if its de Broglie wavelength is 1 µm?

Solution:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

or,

$$v = \frac{h}{m\lambda} = \left(\frac{h}{mc}\right)\frac{c}{\lambda}.$$

For an electron, $\left(\frac{h}{mc}\right) = 2.4 \text{ pm}$.

So

$$v = \frac{(2.4 \text{ pm})}{(1\ \mu\text{m})} \times c = 2.4 \times 10^{-6} c$$

$$= (2.4 \times 10^{-6}) \times (3 \times 10^8 \text{ m/s}) = 720 \text{ m/s}.$$

3. The de Broglie wavelength λ and the kinetic energy E for a highly relativistic electron are related as $\lambda = \alpha/E$. If λ and E represent the numerical values in angstrom and kiloelectronvolt, find the numerical value of α.

Solution: For a highly relativistic electron, the kinetic energy and the linear momentum are related by $E = pc$, a relation strictly true for a photon. Thus the de Broglie wavelength is

$$\lambda = \frac{h}{p} = \frac{hc}{E} = \frac{1240 \text{ eV nm}}{E} = \frac{12.4 \text{ keV Å}}{E}.$$

If E is in keV, λ is angstrom, $\lambda = \frac{12.4}{E}$. Thus $a = 12.4$.

4. x-ray diffraction from a crystal gives a strong peak at an angle of 120° from the incident beam. The x-ray wavelength is 1.5 Å. Find the spacing between the adjacent atomic planes giving rise to this diffraction.

Solution: The angle of the x-ray beams from the planes is $\theta = \left(180^\circ - 120^\circ\right)/2 = 30^\circ$. Strong diffraction peak occurs for

Fig. 3.W1

$$2d\sin\theta = \lambda$$

Thus $$d = \frac{\lambda}{2\sin\theta} = \frac{1.5\text{Å}}{2\sin 30^\circ} = 1.5\text{Å}.$$

5. The wave function of a particle at a given time is

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L} \qquad \text{for} \quad 0 < x < L$$
$$= 0 \qquad \text{otherwise.}$$

Find the probability of finding the particle in the range $L/4 < x < 3L/4$ at this time.

Solution: The probability is

$$\int_{L/4}^{3L/4} |\psi(x)|^2\, dx = \int_{L/4}^{3L/4} \frac{2}{L}\sin^2\frac{\pi x}{L}\, dx$$
$$= \frac{1}{L}\int_{L/4}^{3L/4}\left(1 - \cos\frac{2\pi x}{L}\right)dx$$
$$= \frac{1}{L}\left[x - \frac{L}{2\pi}\sin\frac{2\pi x}{L}\right]_{L/4}^{3L/4} = \frac{1}{L}\left[\frac{L}{2} + \frac{L}{\pi}\right] = 0.82.$$

6. Check if the following function can be a wave function for a realistic state of a particle.

$$\psi(x) = Ae^{-x/a} \qquad \text{for } x > 0$$
$$= -Ae^{+x/a} \qquad \text{for } x < 0.$$

Solution: The given function is plotted in Figure 3.W2. The function is finite everywhere and also square integrable. But it is not continuous at $x = 0$. The value of $\psi(x)$ at $x = 0$ from the expression for $x > 0$ is A, and that from the expression for $x < 0$ is $-A$. Thus the given function does not represent a realistic wave function.

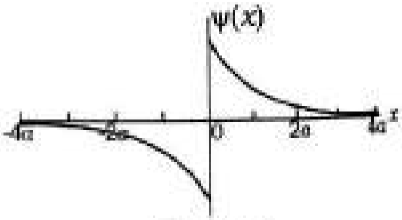


Fig. 3.W2

7. Show that $x\,\delta(x - x_0) = x_0\,\delta(x - x_0)$. Assume x_0 to be a nonzero constant.

Solution: Consider the function $f(x) = \frac{1}{x_0}x\,\delta(x - x_0)$.

At $x = x_0$, $\delta(x - x_0) = \infty$ and so $f(x) = \infty$. (i)

At $x \neq x_0$, $\delta(x - x_0) = 0$ and so $f(x) = 0$. (ii)

Now check the integral of $f(x)$ in the full range.

$$\int_{-\infty}^{\infty} f(x)\ dx = \frac{1}{x_0}\int_{-\infty}^{\infty} x\,\delta(x-x_0)\ dx = \frac{1}{x_0}x_0 = 1. \qquad \text{(iii)}$$

From (i), (ii) and (iii),

$$f(x) = \delta(x-x_0)$$

or,
$$\frac{1}{x_0}x\,\delta(x-x_0) = \delta(x-x_0)$$

or,
$$x\,\delta(x-x_0) = x_0\,\delta(x-x_0).$$

8. Show that $\delta(ax) = \frac{1}{|a|}\delta(x)$ for any nonzero value of a.

Solution: At $x \neq 0$, $ax \neq 0$, so $\delta(ax) = 0$. (i)

At $x = 0$, $ax = 0$, so $\delta(ax) = \infty$. (ii)

Let us calculate $I = \int_{-\infty}^{\infty} \delta(ax)\,dx$.

Put $ax = y$, then $dx = dy/a$. If $a > 0$, y becomes ∞ at $x = \infty$ and becomes $-\infty$ at $x = -\infty$. Thus,

$$I = \frac{1}{a}\int_{-\infty}^{\infty}\delta(y)\,dy = \frac{1}{a}. \qquad \text{(iii)}$$

From (i), (ii) and (iii)

$$\delta(ax) = \frac{1}{a}\delta(x).$$

If $a < 0$, the integration limits are reversed so that $I = -\frac{1}{a}$

giving $$\delta(ax) = -\frac{1}{a}\delta(x).$$

In both cases, $\delta(ax) = \frac{1}{|a|}\delta(x)$.

9. The wave function of a particle at an instant is given as

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad \text{for } x < 0$$
$$= Ce^{-kx} \qquad \text{for } x > 0.$$

Show that $A + B = C$.

Solution: The wave function should be continuous everywhere. Thus $\psi(x)$ at $x = 0$ calculated from the first expression is equal to that from the second expression. This gives

$$A + B = C.$$

EXERCISES

1. The de Broglie wavelength λ of an electron with kinetic energy E is given by $\lambda = a/\sqrt{E}$ for nonrelativistic speeds. If λ and E represent the numerical values in angstrom and electronvolt respectively, find the value of a.
Ans. 12.25

2. Find the de Broglie wavelength of (a) a 1 keV electron (b) a 10 MeV electron (c) a 10 MeV neutron. The energies represent kinetic energy.
Ans. (a) 38.7 pm (b) 0.124 pm (c) 9.04 fm

3. Find the de Broglie wavelength of a thermal neutron ($kT = 0.026$ eV).
Ans. 0.177 nm

4. Find the kinetic energy of an electron whose de Broglie wavelength is 1 Å.
Ans. 150 eV

5. A proton and an electron have the same de Broglie wavelength. If the kinetic energy of the proton is 1.0 keV, find that of the electron.
Ans. 1836 keV

6. A neutron moves at a speed of 3×10^4 m/s. Find its kinetic energy in electronvolt and wavelength in nanometers.
Ans. 4.69 eV, 0.013 nm

7. The resolution of a microscope is roughly the same as the wavelength used for imaging. What should be the kinetic energy of electrons to be used in an electron microscope with resolution of 1.0 nm?
Ans. 15 eV

8. The average inter-particle separation in a noninteracting helium gas at temperature 100 nK is of the order of the de Broglie wavelength of its particles. Estimate the number of particles per cubic centimeter in the gas. [Hint: you can assume that each particle corresponds to a volume d^3 where d is the average interparticle separation.]
Ans: $\approx 10^{10}$

9. If 5 waves completely fit in an orbit of electron in a hydrogen atom, what would be the value of orbital angular momentum (rp) according to Bohr's model? Does it change if it is He⁺ instead of hydrogen atom.
Ans. $5\hbar$, no

10. Lattice planes in a metallic crystal separated by a distance of 2.0 Å diffract an electron beam. The electrons have kinetic energy 100 eV each. Find the angle θ made by the direction of motion of the electrons with the lattice planes for which strong Bragg reflection occurs.
Ans. $\sin^{-1}(0.31)$

11. Prove that (a) $f(x)\delta(x-a) = f(a)\delta(x-a)$ (b) $\delta(x) = \delta(-x)$.

12. Evaluate $\int_a^b \frac{\delta(x-1)\,dx}{x^2+4}$ for (a) $a = 2, b = -4$, (b) $a = -2, b = 4$ (c) $a = 2, b = 4$, (d) $a = -2, b = -4$.
Ans. (a) 1/5 (b) 1/5 (c) 0 (d) 0

13. Which of the followings represent a realistic wave function of a particle? (a) $\psi(x) = Ae^{x^2/a^2}e^{ikx}$ (b) $\psi(x) = Ae^{-|x|/a}e^{ikx}$ (c) $\psi(x) = \frac{A\sin kx}{x^2}$ (d) $\psi(x) = Ae^{-x/a}$ for $x > 0$ and $Ae^{+x/a}$ for $x < 0$.
Ans. (b), (d)

14. The wave function of a particle at a certain time is $\psi(x) = \frac{A}{\sqrt{x^2+a^2}}e^{ikx}$. Find the real positive value of A so that $\psi(x)$ is normalized.
Ans. $\sqrt{a/\pi}$

15. The wave function of a particle at a particular instant is $\psi(x) = Ae^{\gamma|x|}$. Show that A can be taken as $\sqrt{1/\gamma}$ if $\psi(x)$ is normalized.

16. The wave function of a particle at a certain instant is given as $\psi(x) = A\exp\left(-x^2/a^2 + ikx\right)$. If P_1 and P_2 denote the probabilities of finding the particle in the range a to $a + da$ and $2a$ to $2a + da$ respectively, find the rati P_1/P_2.
Ans. e^6

17. Consider a function $\psi(x) = 0$ for $|x|\,)a$, and $= c$ for $|x| \le a$. Can this represent a realistic wave function? If no, why?

Ans. no, it is discontinuous at $x = \pm a$

18. Consider the function $\psi(x) = k_1 + k_2 e^{-x^2/a^2}$ where k_1 and k_2 are nonzero constants. Can this represent a realistic wave function? If not, why?

Ans. no, it is not square integrable

19. A function is written as $\psi(x) = Ae^{(ik+\gamma)x}$ for $x \le 0$ and $\psi(x) = Ae^{(ik-\gamma)x}$ for $x > 0$ where k and γ are positive constants. Can this be a realistic wave function of a particle? If not, why? If yes, find the probability of finding the particle in the range $-\frac{1}{\gamma} < x < \frac{1}{\gamma}$.

Ans. yes, 0.86

20. The wave function of a particle is given as

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\frac{3\pi x}{L} \quad \text{for } 0 < x < L$$

$$= 0 \quad \text{otherwise.}$$

Find the probability of finding the particle in the range $L/4 < x < 3L/4$.

Ans. $\frac{1}{2} - \frac{1}{3\pi}$

21. The wave function of a particle is given as $\psi(x) = \frac{1}{\sqrt{a}} e^{-|x|/a}$. (a) Find the probability of finding the particle in the range $-a < x < a$. (b) Find the value of b so that the probability of finding the particle in the range $-b < x < b$ is 0.5.

Ans. (a) $\frac{e^2 - 1}{e^2}$ (b) $\frac{a}{2}\ln 2$

4

Position and Linear Momentum of a Particle

The rules for a quantum system, such as an electron, are very different from those of classical physics. At any given time, a wave function $\psi(x)$ is associated with the particle. This wave function contains all the information about the particle that is possible to have at that time. That is why we say that $\psi(x)$ describes the "state" of the particle. In this chapter I will be telling you what information about position and linear momentum can be obtained if the wave function $\psi(x)$ is given.

4.1 Position distribution and expansion in position eigenfunctions

If the wave function of a particle at a given time is $\psi(x)$, the probability of finding the particle at this time in the range x to $x + dx$ is $|\psi(x)|^2\,dx$. I assume that $\psi(x)$ is normalized. Figure 4.1 shows an example where the wave function is such that $|\psi(x)|^2$ has appreciable values only in the range x_1 to x_2. Hence the particle does not have a definite position at this instant. All positions from x_1 to x_2 are simultaneously available to the particle. However, if you measure the position, you don't get all values from x_1 to x_2 simultaneously. You will get only one value which could be anything between x_1 and x_2. Also, all values are not equally likely. The probability of getting a value between x and $x + dx$ is $|\psi(x)|^2\,dx$ which is different for different values of x. Suppose, you have a large number of separate systems, each having a particle in the same state $\psi(x)$. If you measure position of each of these particles, you will get different values for different particles. The number of particles giving you values between x and $x + dx$ will be about $N\,|\psi(x)|^2\,dx$ where N is the total number of systems. Though all particles before measurement were in identical states, and identical measurements were made, the results are different.

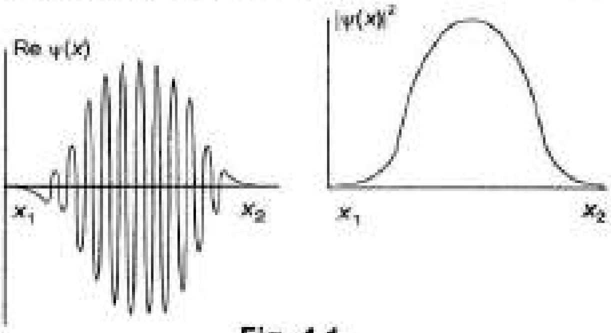


Fig. 4.1

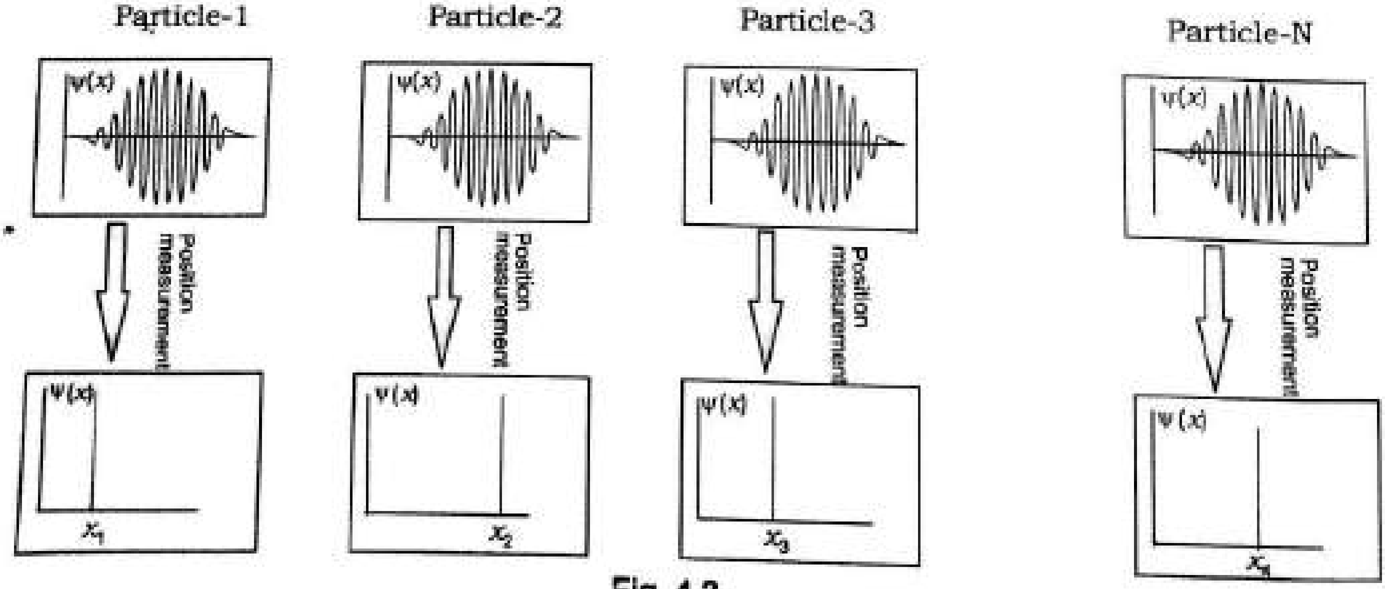


Fig. 4.2

Once a position measurement is made on a particle in state $\psi(x)$ and a particular result x_i is obtained, the wave function of the particle abruptly changes to a delta function $A\delta(x-x_i)$, which is the eigenfunction of position corresponding to the position x_i. Figure 4.2 shows this schematically.

Any wave function $\psi(x)$ can be expanded as a combination of delta functions $\delta(x-x_0)$ with various values of x_0. I will show you that there is an intimate relation between the coefficients of expansion of $\psi(x)$ and the probability density. You remember,

$$\int_{-\infty}^{\infty} f(x)\,\delta(x-x_0)\,dx = f(x_0).$$

Using this you can write any wave function $\psi(x)$ as

$$\psi(x) = \int_{-\infty}^{\infty} \psi(x_0)\,\delta(x-x_0)\,dx_0 .$$

Writing the state represented by $\delta(x-x_0)$ as $|x_0\rangle$ (basis position eigenfunction) and that represented by $\psi(x)$ as $|\psi(x)\rangle$,

$$|\psi(x)\rangle = \int_{-\infty}^{\infty} [\psi(x_0)](|x_0\rangle)\,dx_0 . \tag{4.1}$$

Integration is a process of summation. Thus Equation 4.1 gives the expansion of $|\psi(x)\rangle$ in terms of the functions $|x_0\rangle$ which are the eigenfunctions of position measurement with properly defined multiplying constants. $\psi(x_0)$ is the expansion coefficient of $|x_0\rangle$ in this expansion. You also know that the probability of finding the position between x_0 and x_0+dx_0 is $|\psi(x_0)|^2\,dx_0$. Thus the probability of finding the value of x in the range x_0 to x_0+dx_0 can be obtained by expanding $|\psi(x)\rangle$ in terms of the eigenfunctions of position measurement, finding the expansion coefficient of $|x_0\rangle$, squaring its absolute value and multiplying by dx_0.

This is an application of a general procedure involving continuously varying quantities. Suppose, there is a physically measurable quantity λ which can take all values from $-\infty$ to $+\infty$ in a continuous fashion. Corresponding to each possible value λ_0, there is a pure state of λ measurement having a particular wave function. This wave function is called eigenfunction of λ corresponding to the value λ_0. I denote this eigenfunction, with properly defined multiplying constant, by $|\lambda_0\rangle$. At any given time, the particle has a state $|\psi(x)\rangle$ given by the wave function $\psi(x)$. You can expand this state in terms of the eigenfunctions $|\lambda_0\rangle$ as

$$|\psi(x)\rangle = \int_{-\infty}^{\infty} |\lambda_0\rangle\,a(\lambda_0)\,d\lambda_0 . \tag{4.2}$$

The expansion coefficient corresponding to the term $|\lambda_0\rangle$ in this expansion is $a(\lambda_0)$. The probability of finding the value of λ in the range λ_0 to $\lambda_0+d\lambda_0$ is equal to $|a(\lambda_0)|^2\,d\lambda_0$. Go back to Equation 4.1 and the paragraph following it and see that position x follows this general description for continuous variables.

4.2 Expansion in terms of momentum eigenfunctions

In the previous section you saw how a general wave function $\psi(x)$ can be expanded in terms of the basis position eigenfunctions $|x_0\rangle$. You can also expand $\psi(x)$ in terms of the basis momentum eigenfunctions $|p_0\rangle$. Momentum is also a continuous variable that can take all values from $-\infty$ to $+\infty$.

The basis eigenfunction corresponding to the value p_0 is $\frac{1}{\sqrt{2\pi\hbar}}\, e^{\frac{i}{\hbar}p_0 x}$.

The expansion of $|\psi(x)\rangle$ in terms of $|p_0\rangle$'s can be written as

$$|\psi(x)\rangle = \int_{-\infty}^{\infty} a(p_0)\,|p_0\rangle\, dp_0 \tag{4.3}$$

$a(p_0)$ being the expansion coefficient of $|p_0\rangle$. Thus,

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} a(p_0)\, e^{\frac{i}{\hbar}p_0 x}\, dp_0 . \tag{4.4}$$

The expansion of $|\psi(x)\rangle$ in terms of $|p_0\rangle$ given in Equation 4.3 means, $|\psi(x)\rangle$ can be thought of as containing all these $|p_0\rangle$'s in it. A particular $|p_0\rangle$ corresponds to a particular momentum p_0. As $|\psi(x)\rangle$ contains so many $|p_0\rangle$'s, the momentum of the particle has so many possible values at this instant. We say that the momentum is not definite in the state $\psi(x)$. Of course if you measure the momentum, you will get only one value of p. But which value; that no one can tell before the measurement. Only after the measurement is made, you know the value of momentum. Be very careful in interpreting the previous sentence. If you get a value p_1 of momentum in your measurement, it does not mean that momentum was p_1 before the measurement. As you know, measurement disturbs the system. Momentum is p_1 after the measurement and not before the measurement. There is no way to know the momentum before the measurement. If you prepare a large number of identical particles in the same state $\psi(x)$ and make identical momentum measurement on each of them, you will get different values of momentum for different particles. The probability of getting a value in the range p_0 to $p_0 + dp_0$ will be $|a(p_0)|^2\, dp_0$. This means, if the number of systems N is large, in about $N|a(p_0)|^2\, dp_0$ cases you will find a value of momentum in the range p_0 to $p_0 + dp_0$. And if a value p_0 is obtained, the wave function of the particle gets abruptly changed

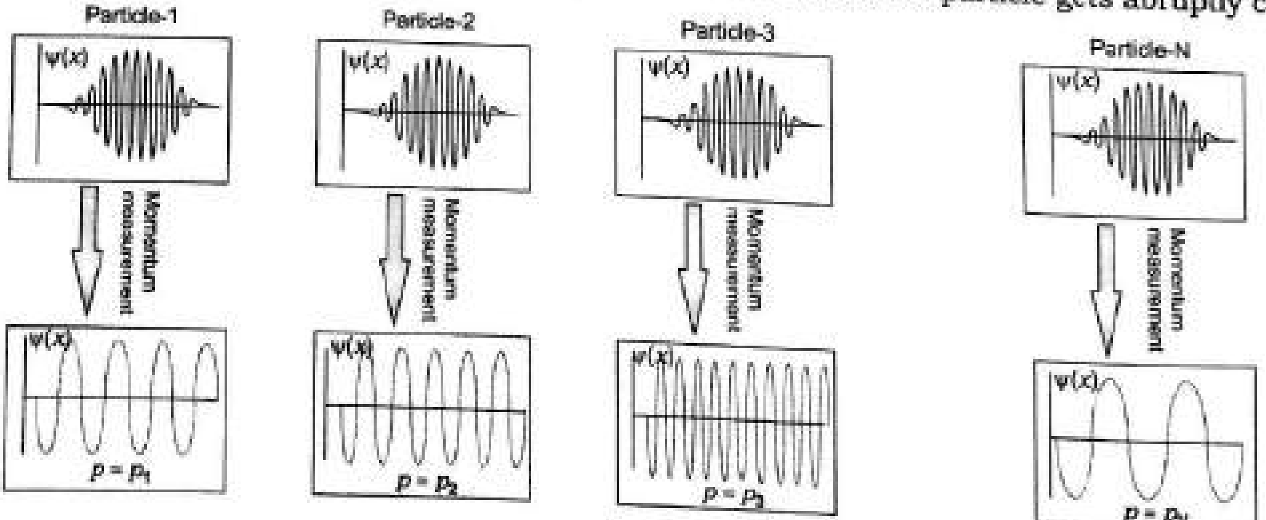


Fig. 4.3

from $\psi(x)$ to the corresponding momentum eigenfunction.

I have depicted the above ideas in Figure 4.3. You might say it is not a realistic representation. The wave functions are in general complex and graphical representation is often not possible. The momentum eigenfunction $|p_0\rangle = \frac{1}{\sqrt{2\pi\hbar}}\, e^{\frac{i}{\hbar}p_0 x}$ is indeed complex and cannot be shown as a graph like that in Figure 4.3. But it is a plane wave and by the drawings I wish to convey to you that the wave packet type wave function $\psi(x)$ abruptly changes to a plane wave when momentum measurement is made.

Equation 4.4 can also be written as,

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} a(p)\, e^{\frac{i}{\hbar}px}\, dp\,. \tag{4.5}$$

The question is, given $\psi(x)$, how one gets $a(p)$. There are mathematical theorems, under the heading of "Fourier transformations" which help us in finding $a(p)$ if $\psi(x)$ is given. The expression is,

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x)\, e^{-\frac{i}{\hbar}px}\, dx\,. \tag{4.6}$$

Note that in Equation 4.5, the integration is performed over p. And it is a definite integration. You put the limits of p after integration. So the final form does not contain p, and you get $\psi(x)$, which depends only on x. On the other hand, the integration in Equation 4.6 is performed over x and the limits of x are put after integration. Hence you get $a(p)$ which depends only on p. The function $a(p)$ is called the *momentum wave function* or *momentum distribution function* of the particle.

4.3 An example of expansion of wave function

Let me give you an example of expansion of wave function in terms of plane waves, that is, momentum eigenfunctions. Suppose the wave function of a particle at $t = 0$ is

$$\psi(x) = A\, e^{-c|x| + \frac{i}{\hbar}p_0 x}.$$

This is a complex function and cannot be plotted as a ψ versus x graph. The real and imaginary parts are

$$\mathrm{Re}\left[\psi(x)\right] = A\, e^{-c|x|} \cos\left(\frac{p_0}{\hbar}x\right)$$

and $$\mathrm{Im}\left[\psi(x)\right] = A\, e^{-c|x|} \sin\left(\frac{p_0}{\hbar}x\right).$$

Each of the two parts is an oscillating function of x with decaying amplitude (Figure 4.4). The amplitude decays exponentially and becomes negligible for $|x|$ greater than few times of $1/c$. The wave

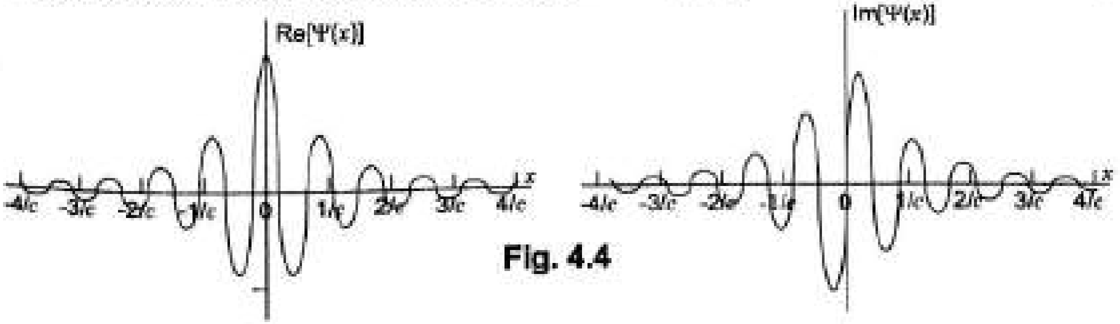


Fig. 4.4

function is thus confined to a finite range of x, having a width of the order of $1/c$. This is an example of a wave packet.

Position is not definite for this particle. The probability density is $|\psi(x)|^2 = |A|^2 e^{-2c|x|}$. The probability of finding the particle near $x = 0$ is the largest and decreases as you look for the particle away from $x = 0$.

Let me expand this wave function in terms of plane waves, i.e., the momentum eigenfunctions. This expansion is obtained from Equation 4.5, I have to find the expansion coefficient $a(p)$. And that can be obtained from Equation 4.6.

$$
\begin{aligned}
a(p) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x)\, e^{-\frac{i}{\hbar}px}\, dx \\
&= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} A\, e^{-c|x| + \frac{i}{\hbar}(p_0 - p)x}\, dx \\
&= \frac{A}{\sqrt{2\pi\hbar}} \int_{-\infty}^{0} e^{cx + \frac{i}{\hbar}(p_0 - p)x}\, dx + \int_{0}^{\infty} e^{-cx + \frac{i}{\hbar}(p_0 - p)x}\, dx \\
&= \frac{2Ac\hbar^2}{\sqrt{2\pi\hbar}} \frac{1}{(p - p_0)^2 + \hbar^2 c^2}.
\end{aligned}
$$

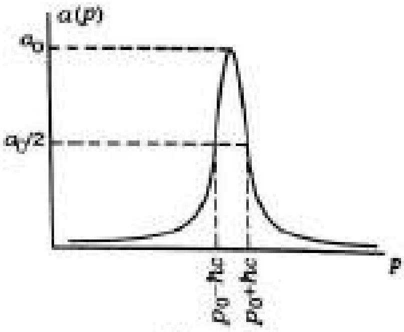


Fig. 4.5

This is a function of p and I show its dependence on p in Figure 4.5. Such a function is called a Lorentzian function. The maximum value of $a(p)$ occurs at $p = p_0$. The value falls to half of the maximum at $p_0 \pm \hbar c$. Thus the wave function $\psi(x)$ is obtained by superposing plane waves corresponding to momenta values in the range few times $\hbar c$, centered at p_0.

4.4 The factor of $\frac{1}{\sqrt{2\pi\hbar}}$ in $|p\rangle$

The momentum eigenfunction $|p\rangle$ is defined as

$$|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}px}.$$

Why do we use the factor $\frac{1}{\sqrt{2\pi\hbar}}$? Let me justify it using dimensions. Let square bracket denote the dimensions. Then,

$$\left[|\psi(x)|^2\, dx\right] = 1 \quad \Rightarrow \quad [\psi(x)] = \left[\frac{1}{\sqrt{L}}\right]$$

and $$\left[|a(p)|^2\, dp\right] = 1 \quad \Rightarrow \quad [a(p)] = \left[\frac{1}{\sqrt{P}}\right].$$

Also, $$[\psi(x)] = [|p_0\rangle][a(p)][dp].$$

This gives,

$$[|p_0\rangle] = \frac{[\psi(x)]}{[a(p)][dp]} = \left(\frac{1}{\sqrt{L}} \times \frac{\sqrt{p}}{p}\right) = \left(\frac{1}{\sqrt{p.L}}\right).$$

Now, $p.L$ has the dimensions of angular momentum. Thus $|p_0\rangle$ must have dimensions of (angular momentum)$^{-1/2}$. And the angular momentum most familiar to a quantum physicist is the Planck's constant. Thus $\frac{1}{\sqrt{2\pi\hbar}}$ makes the dimensions correct.

4.5 The wave function as a vector

The wave function of a particle is continuous, finite everywhere and square integrable. The wave function tells me everything about the particle (at that instant) that is possible to know. We therefore say that the wave function defines the state of the particle. Let us collect all possible wave functions of a particle and call the set of these wave functions as F. Such a set is called the *state space* of the particle because each member of this set is a possible wave function representing a particular state of the particle. Many of the mathematical characteristics of this set are the same as those in the set of all geometrical vectors that you have studied in mathematics or physics. Two vectors may be added to get a third vector. Similarly two functions may be added to get a third function. A vector can be multiplied by a number to get another vector. Similarly a function can be multiplied by a number to get another function. Similarly for other properties. The set F of all possible wave functions is an example of *linear vector space*. The wave functions themselves are sometimes called *state vectors*.

It is not necessary to represent the states as wavefunctions to construct the state space. You can think of the collection of all possible states of the particle in their abstract form. That is the state space $|\psi\rangle, |\phi\rangle$ etc will be the state vectors.

An important quantity related to the geometrical vectors is the scalar product **a.b** of two vectors **a** and **b**. This product is just a number. We also define the scalar product of two state vectors or wave functions $\psi_1(x)$ and $\psi_2(x)$. The scalar product is written as $\langle\psi_1|\psi_2\rangle$ and is defined as

$$\langle\psi_1|\psi_2\rangle = \int_{-\infty}^{\infty} \psi_1^*(x)\,\psi_2(x)\,dx. \tag{4.7}$$

The complex conjugate of the first function $\psi_1(x)$ is multiplied by the second function $\psi_2(x)$. This is integrated over the full range of x. As this is a definite integral, it is just a number. So, the scalar product of two functions $\psi_1(x)$ and $\psi_2(x)$ is a number. This number may be complex.

As $|\psi\rangle$ is read as ket ψ, $\langle\psi|$ is read as bra ψ. The words bra and ket are left and right parts of the word bracket. You can think of the scalar product $\langle\psi_1|\psi_2\rangle$ as the product of the bra $\langle\psi_1|$ and the ket $|\psi_2\rangle$. In rigorous formulation of quantum mechanics, there is a much deeper significance of bra vectors, but I will not discuss that. For us it will be only a symbol used to indicate the first function in a scalar product. $\langle\psi_1|\psi_2\rangle$ is also called scalar product of the state $|\psi_1\rangle$ with $|\psi_2\rangle$.

The scalar product is not commutative. From the defining Equation 4.7, it is seen that

$$\langle\psi_1|\psi_2\rangle = \langle\psi_2|\psi_1\rangle^*. \tag{4.8}$$

Only if the scalar product is a real number, $\langle\psi_1|\psi_2\rangle = \langle\psi_2|\psi_1\rangle$.

The magnitude of a geometrical vector is given by $|\mathbf{a}| = (\mathbf{a}.\mathbf{a})^{1/2}$. Take the scalar product of the vector a with itself and you get the square of the magnitude of **a**. We define a similar quantity *norm* for the functions in F. The scalar product of a function $\psi(x)$ with itself is the square of the norm of $\psi(x)$.

$$\text{Norm} = \left[\langle\psi|\psi\rangle\right]^{1/2} \tag{4.9}$$

$$= \left[\int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx\right]^{1/2}$$

$$= \left[\int_{-\infty}^{\infty} |\psi(x)|^2\,dx\right]^{1/2}. \tag{4.10}$$

Note that it is a real, nonnegative number. It can never be negative and is zero only if $\psi(x)$ is zero for all x. Such a function (zero everywhere) cannot represent a wave function and is of no interest to us.

A geometrical vector having unit magnitude is called *unit vector*. A wave function $\psi(x)$ having unit norm is called a *normalized wave function*. We generally use normalized wave functions for the description of a quantum system.

If the scalar product of two geometrical vectors **a** and **b** is zero, they are called orthogonal to each other. If the scalar product of two wave functions is zero, they are also called orthogonal to each other. Thus $\psi_1(x)$ and $\psi_2(x)$ are orthogonal to each other if

$$\langle\psi_1|\psi_2\rangle = \int_{-\infty}^{\infty} \psi_1^*(x)\psi_2(x)\,dx = 0.$$

The geometrical vector space is three-dimensional. If you choose three unit vectors $\hat{\mathbf{i}}, \hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$, orthogonal to each other, you can express any vector **a** as their linear combination

$$\mathbf{a} = a_x\hat{\mathbf{i}} + a_y\hat{\mathbf{j}} + a_z\hat{\mathbf{k}}.$$

The vectors $\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}$ are called the *basis vectors* for the geometrical vector space. The choice of the basis vectors is not unique. You can take any three orthogonal unit vectors and that will form a basis. But you always need three such vectors to describe all possible vectors and that is why you say that the geometrical vector space is three-dimensional.

The state space F is, in general, infinite-dimensional. We need infinite number of functions to form a basis for F. Let me write the basis functions as $|\phi_1\rangle, |\phi_2\rangle, |\phi_3\rangle, \ldots$. The basis functions are so chosen that they are orthogonal to each other, and also the norm of each of them is unity. Such a basis is called *orthonormal basis*. The orthonormalization condition may be written as $\langle\phi_i|\phi_j\rangle = \delta_{ij}$ where δ_{ij} is 1 if $i = j$ and zero otherwise. This quantity δ_{ij} is called *Kroneckar delta*.

Any state vector $|\psi\rangle$ can be written as

$$|\psi\rangle = \sum_i c_i|\phi_i\rangle. \tag{i}$$

The expression $\sum_i c_i|\phi_i\rangle$ is called a linear combination of $|\phi_i\rangle$'s. You multiply $|\phi_i\rangle$'s by constants and add. This becomes a linear combination. The number c_i may be called the "component" of $|\psi\rangle$ in the "direction" of $|\phi_i\rangle$. These terms are taken from those commonly used for geometrical vectors. When you write

$$\mathbf{a} = a_x\hat{\mathbf{i}} + a_y\hat{\mathbf{j}} + a_z\hat{\mathbf{k}}$$

a_x, a_y, a_z are called components of **a** in the directions of **i**, **j** and **k** respectively. You can write these components as $a_x = \mathbf{i}.\mathbf{a}$, $a_y = \mathbf{j}.\mathbf{a}$, $a_z = \mathbf{k}.\mathbf{a}$. To get the component of **a** in a given direction, you take the scalar product of the unit vector in that direction with **a.** You can write similar expressions for the components of $|\psi\rangle$.

$$c_j = \langle \phi_j | \psi \rangle \qquad \text{(ii)}$$

that is, take the scalar product of the basis function $|\phi_j\rangle$ with the given function $|\psi\rangle$ to get c_j . You can verify this equation easily. We have,

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle$$

or

$$\langle \phi_j | \psi \rangle = \sum_i c_i \langle \phi_j | \phi_i \rangle . \qquad \text{(iii)}$$

The scalar product $\langle \phi_j | \phi_i \rangle$ is zero if $i \neq j$ and 1 if $i = j$. If you open up the summation in (iii), writing each term separately corresponding to i = 1, 2, 3, ... , only one of the terms will survive when i will be equal to j. And that term will be just c_j verifying (ii).

The kind of basis I have introduced above is called a *discrete basis*. This is because you can count them, $|\phi_1\rangle, |\phi_2\rangle, |\phi_3\rangle$, etc. Remember, each of these is a function of x, but you can still count, this is the first function, this is the second, and so on. It is also possible to have a continuous set of functions as a basis. In such a case, the basis functions are not indexed by a discrete label i but by a variable which can take any value from $-\infty$ to $+\infty$. The set of Dirac delta functions $\delta(x - x_0)$, also written as $|x_0\rangle$ (this represents the state of the particle with definite position), is such a basis. You have infinite number of delta functions, each centered at a different value of x_0 . You cannot label them as the first function, the second function, etc., because between any two unequal values of x_0 there are infinitely many other values. But you can write any function $\psi(x)$ in terms of these delta functions. Such a basis is called a *continuous basis*.

Note that $|x_0\rangle$ are themselves not part of the state space, as they do not represent state of any realistic system. But any realistic state can be represented as a linear combination of these states.

In the expansion of $|\psi\rangle$ in terms of the basis functions in equation (i) above, I used the discrete index i for summation. For a continuous basis, the expansion will be an integration over the whole range of the continuous label describing the basis. For example, using $|x_0\rangle$ basis,

$$|\psi\rangle = \int_{-\infty}^{\infty} \psi(x_0) |x_0\rangle \, dx_0 .$$

In this expansion, $\psi(x_0)$ is the "component" of $|\psi\rangle$ in the direction of $|x_0\rangle$.

The plane waves $|p_0\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar} p_0 x}$ form another continuous basis. Here p_0 is the continuous label, which can take any value from $-\infty$ to $+\infty$. Any state $|\psi\rangle$ can be written as

$$|\psi\rangle = \int_{-\infty}^{\infty} a(p_0) |p_0\rangle \, dp_0 .$$

Here $a(p_0)$ is the component of $|\psi\rangle$ along $|p_0\rangle$. Like $|x_0\rangle$, the basis $|p_0\rangle$ also does not belong to the state space. In general, if $|\lambda\rangle$ is a continuous basis, where λ can take any value from $-\infty$ to $+\infty$, we can write

$$|\alpha\rangle = \int_{-\infty}^{\infty} c(\lambda)|\lambda\rangle\, d\lambda .$$

Is such a continuous basis orthonormal? The basis functions can be chosen to be orthogonal to each other but their normalization is not assured. You remember, the delta functions and the plane wave functions are not square integrable and hence cannot be normalized. Orthonormality is given a slightly different meaning for continuous basis. A continuous basis $|\lambda\rangle$ is called orthonormal if

$$\langle\lambda_1|\lambda_2\rangle = \delta(\lambda_1 - \lambda_2) . \tag{4.11}$$

What does this equation mean? If $\lambda_1 \neq \lambda_2$, i.e., if I take two different basis functions $|\lambda_1\rangle$ and $|\lambda_2\rangle$, the scalar product is zero. But if $\lambda_1 = \lambda_2$, i.e., I am calculating square of the norm of a basis function $|\lambda_1\rangle$, it is infinity.

Example 4.1

Let $|\psi\rangle = \int_{-\infty}^{\infty} c(\lambda)|\lambda\rangle\, d\lambda$ *where* $|\lambda\rangle$*'s form a continuous orthonormal basis. Show that* $c(\lambda) = \langle\lambda|\psi\rangle$.

Solution: Let me change the dummy variable λ to μ and write $|\psi\rangle = \int_{-\infty}^{\infty} c(\mu)|\mu\rangle\, d\mu$.

Then, $\langle\lambda|\psi\rangle = \int_{-\infty}^{\infty} c(\mu)\langle\lambda|\mu\rangle\, d\mu$

$$= \int_{-\infty}^{\infty} c(\mu)\,\delta(\lambda-\mu)\, d\mu = c(\lambda) .$$

Often the continuous basis functions are not themselves valid wave functions, i.e., they do not belong to the set F of all possible wave functions. $|x_0\rangle$, $|p_0\rangle$ are not normalizable and do not represent wave functions for any realistic situation. But any realistic wave function can be expanded in terms of these.

4.6 You learned in this chapter

- Any wave function $\psi(x)$ can be expanded in terms of the position eigenfunctions $\delta(x - x_0)$. The expansion coefficients are $\psi(x_0)$ and the probability of getting the position x in the range x_0 to $x_0 + dx_0$ is $|\psi(x_0)|^2\, dx_0$.
- If identical particles in identical initial states, given by the same wave function $\psi(x)$, are subjected to identical position measurements, different values of x can be obtained in different measurements.
- The wave function $\psi(x)$ abruptly changes to $|x_0\rangle$, i.e., $\delta(x - x_0)$, if the measurement gives x_0 as the position.

- Any wave function $\psi(x)$ can be expanded in terms of the momentum eigenfunctions $|p\rangle$, that is, plane waves with different wavelengths.
- If $|\psi\rangle = \int_{-\infty}^{\infty} a(p)|p\rangle\, dp$ then $a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x)\, e^{-\frac{i}{\hbar}px} \psi(x)\, dx$.
- The probability of getting the momentum value between p_0 and $p_0 + dp_0$ is $|a(p_0)|^2\, dp_0$.
- If the momentum measurement on a particle in a state $\psi(x)$ gives a value p_0, the wave function abruptly changes to $|p_0\rangle$, i.e., a plane wave with wavelength h/p_0.
- The scalar product of the wave function $\psi_1(x)$ with $\psi_2(x)$ or, state $|\psi_1\rangle$ with $|\psi_2\rangle$, is defined as

  $$\langle \psi_1 | \psi_2 \rangle = \int_{-\infty}^{\infty} \psi_1^*(x)\, \psi_2(x)\, dx$$

  and is noncommutative.
- If $\langle \psi_1 | \psi_2 \rangle$ is zero, $\psi_1(x)$ and $\psi_2(x)$ are called orthogonal.
- The norm of a wave function $\psi(x)$ is defined to be $\langle \psi | \psi \rangle^{1/2}$.
- If $|\phi_i\rangle$ is an orthonormal basis for the state space and $|\psi\rangle = \sum_i c_i |\phi_i\rangle$, then $c_i = \langle \phi_i | \psi \rangle$. This quantity is called the component of $|\psi\rangle$ along $|\phi_i\rangle$.
- Orthonormalization condition for a discrete basis $|\phi_i\rangle$ is $\langle \phi_i | \phi_j \rangle = \delta_{ij}$, and for a continuous basis $|\lambda\rangle$ it is $\langle \lambda_1 | \lambda_2 \rangle = \delta(\lambda_1 - \lambda_2)$.

Solved Problems

1. Suppose (hypothetically) that the wave function of a particle is given as $\psi(x) = Ae^{\frac{i}{\hbar}p_0 x}$. Find the momentum wave function $a(p)$.

Solution:

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x) e^{-\frac{i}{\hbar}px} dx$$

$$= \frac{A}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}p_0 x} e^{-\frac{i}{\hbar}px} dx = \frac{A}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(p_0 - p)x} dx.$$

Write $(p_0 - p) = k\hbar$. The integration becomes,

$$a(p) = \frac{A}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ikx} dx.$$

But you know that $\int_{-\infty}^{\infty} e^{ikx}dx = 2\pi\,\delta(k)$.

Thus
$$a(p) = \sqrt{\frac{2\pi}{\hbar}}A\,\delta(k)$$
$$= \sqrt{\frac{2\pi}{\hbar}}A\,\delta\left(\frac{p_0 - p}{\hbar}\right)$$
$$= \sqrt{2\pi\hbar}A\,\delta(p - p_0) = B\,\delta(p - p_0).$$

What does this tell? $a(p)$ is zero for all values of p other than p_0. This is expected because the wave function $\psi(x)$ itself is a momentum eigenfunction and hence the particle has a definite momentum p_0.

2. The wave function of a particle is given as

$$\psi(x) = \frac{2}{a^{3/2}}x\,e^{-x/a} \quad \text{for} \quad x > 0$$
$$= 0 \quad \text{for} \quad x \le 0.$$

(a) Sketch the wave function. (b) Find $a(p)$ and $|a(p)|^2$. (c) Which value of momentum is most probable?

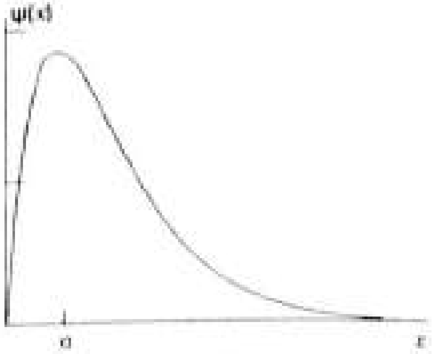


Fig. 4.W1

Solution: **(a)** The wave function is zero for $x \le 0$. Also, at $x = \infty$, the wave function is zero. For all positive values of x, $\psi(x)$ is positive.

$$\frac{d\psi}{dx} = \frac{2}{a^{3/2}}\left(1 - \frac{x}{a}\right)e^{-x/a}$$

which is zero at $x = a$. Thus $\psi(x)$ increases from zero at $x = 0$, becomes maximum at $x = a$ and again decreases to zero at $x = \infty$. The shape is sketched in Figure 4.W1.

(b)
$$a(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(x)\,e^{-\frac{i}{\hbar}px}dx$$
$$= \frac{1}{\sqrt{2\pi\hbar}}\frac{2}{a^{3/2}}\int_0^{\infty} x\,e^{-x/a}e^{-\frac{i}{\hbar}px}dx$$
$$= \frac{1}{\sqrt{2\pi\hbar}}\frac{2}{a^{3/2}}\int_0^{\infty} x\,e^{-\left(\frac{1}{a}+\frac{i}{\hbar}p\right)x}dx.$$

The integration can be easily performed using 'integration by parts', giving,

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}}\frac{2}{a^{3/2}}\frac{1}{\left(-\frac{ip}{\hbar} - \frac{1}{a}\right)^2}$$
$$= \sqrt{\frac{2\hbar^3 a}{\pi}}\frac{1}{(ipa + \hbar)^2}.$$

Thus,
$$|a(p)|^2 = a(p) \times a^*(p)$$

$$= \frac{2\hbar^3 a}{\pi} \frac{1}{\left(p^2 a^2 + \hbar^2\right)^2}.$$

(c) $|a(p)|^2$ is maximum when $p = 0$. Thus $p = 0$ is the most probable value of momentum.

3. The momentum distribution function of a particle is given as $a(p) = \frac{1}{\sqrt{d}}\exp(-|p|/d)$ where d is a constant.

- **(a) Check that $\int_{-\infty}^{\infty} |a(p)|^2 dp = 1$.**
- **(b) Find the value of b so that the probability of finding the momentum in the range $-b < p < b$ is 90%.**
- **(c) Sketch the function $a(p)$ and study the effect on it as d is increased or decreased.**
- **(d) Find the wave function $\psi(x)$ and sketch it as a function of x.**
- **(e) Study the effect on $\psi(x)$ as d is increased or decreased.**

Solution: (a)
$$\int_{-\infty}^{\infty} |a(p)|^2 dp = \int_{-\infty}^{\infty} \frac{1}{d}\exp(-2|p|/d)\,dp$$
$$= \int_{-\infty}^{0} \frac{1}{d}\exp(2p/d)\,dp + \int_{0}^{\infty} \frac{1}{d}\exp(-2p/d)\,dp$$
$$= 2\int_{0}^{\infty} \frac{1}{d}\exp(-2p/d)\,dp = 1.$$

(b) The probability of finding the momentum in the range $-b < p < b$ is

$$\int_{-b}^{b} |a(p)|^2 dp = 2\int_{0}^{b} \frac{1}{d}\exp(-2p/d)\,dp = 1 - \exp(-2b/d).$$

According to the question, this should be 0.90. So,

$$1 - \exp(-2b/d) = 0.90$$

or

$$b = \frac{d}{2}\ln 10 = 1.15\,d.$$

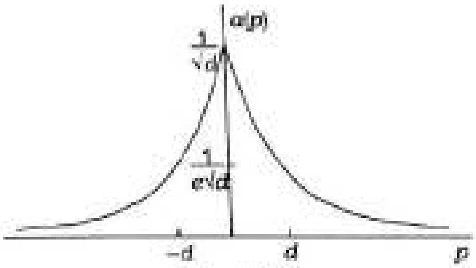


Fig. 4.W2

(c) The sketch of $a(p)$ is shown in Figure 4.W2. The maximum value of $a(p)$ is $1/\sqrt{d}$. As the value of d is increased, this maximum goes down. As the area under $|a(p)|^2$ is fixed (unity), the distribution must become wider in this case. You can also recognize this from the fact that at $p = \pm d$, the value of $a(p)$ falls to $1/e$ of its maximum value.

If d is decreased, the maximum value increases and the distribution gets narrower.

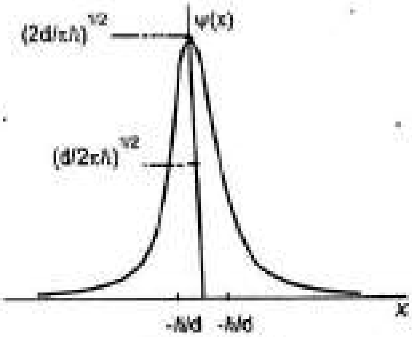


Fig. 4.W3

(d)
$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} a(p)\, e^{\frac{i}{\hbar}px}\, dp$$
$$= \frac{1}{\sqrt{2\pi\hbar d}} \int_{-\infty}^{\infty} e^{-|p|/d}\, e^{\frac{i}{\hbar}px}\, dp$$

$$= \sqrt{\frac{2\hbar^3}{\pi d^3}} \frac{1}{x^2 + (\hbar / d)^2}.$$

The sketch of $\psi(x)$ is shown in Figure 4.W3.

(e) $\psi(x)$ is a Lorentzian curve centered at $x = 0$ and falls to half its maximum value at $x = \pm\hbar/d$. The maximum value itself is (at $x = 0$), $\sqrt{2d/(\pi\hbar)}$ as suggested in Figure 4.W3. As d increases the amplitude increases and the width decreases. On the other hand if d decreases, the amplitude decreases and the width increases. Compare with the case of $a(p)$.

4. The wave function of a particle is given as

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\frac{\pi x}{L} \text{ for } 0 < x < L$$
$$= 0 \text{ otherwise.}$$

Find the probability of its momentum being in the range $\frac{2\hbar}{L}$ to $\frac{2\hbar}{L} + \frac{2\hbar}{100L}$ where h is Planck's constant. You can treat $\frac{2\hbar}{100L}$ as a small quantity.

Solution: The momentum distribution function $a(p)$ is

$$a(p) = \frac{\sqrt{2}}{\sqrt{2\pi\hbar L}} \int_0^L e^{-\frac{i}{\hbar}px} \sin\frac{\pi x}{L}\, dx$$

$$= -e^{-\frac{ipL}{2\hbar}} \frac{2\pi}{L\sqrt{\pi\hbar L}} \frac{\cos\frac{pL}{2\hbar}}{\left(\frac{\pi}{L}\right)^2 - \left(\frac{p}{\hbar}\right)^2}$$

Thus
$$|a(p)|^2 = \frac{4\pi}{\hbar L^3} \frac{\cos^2\left(\frac{pL}{2\hbar}\right)}{\left[\left(\frac{\pi}{L}\right)^2 - \left(\frac{p}{\hbar}\right)^2\right]^2}.$$

Assuming $\frac{2\hbar}{100L}$ to be a small quantity; the probability of momentum being in the range $\frac{2\hbar}{L}$ to $\frac{2\hbar}{L} + \frac{2\hbar}{100L}$ is

$$|a(p)|^2\, dp = \frac{4\pi}{\hbar L^3} \frac{\cos^2\left(\frac{2\hbar}{L} \times \frac{L}{2\hbar}\right)}{\left[\left(\frac{\pi}{L}\right)^2 - \left(\frac{2\hbar}{L\hbar}\right)^2\right]^2} \times \frac{2\hbar}{100L}$$

$$= \frac{16\pi^2}{100L^4\left[\frac{15\pi^2}{L^2}\right]^2} = \frac{16}{22500\pi^2}.$$

5. Show that $\langle x_1 | x_2 \rangle = \delta(x_1 - x_2)$ **where** $|x_1\rangle = \delta(x - x_1)$ **and** $|x_2\rangle = \delta(x - x_2)$.

Solution: $$\langle x_1|x_2\rangle = \int_{-\infty}^{\infty} [\delta(x-x_1)]^* [\delta(x-x_2)]\,dx$$

$$= \int_{-\infty}^{\infty} \delta(x-x_1)\,\delta(x-x_2)\,dx$$

$$= \int_{-\infty}^{\infty} f(x)\,\delta(x-x_1)\,dx$$

where $f(x)=\delta(x-x_2)$. But this integration is equal to $f(x_1)$ which is equal to $\delta(x_1-x_2)$.

6. Show that the wave functions $\psi_1(x) = Ae^{-x^2/a^2}$ and $\psi_2(x) = Bxe^{-x^2/a^2}$ are orthogonal to each other.

Solution: The scalar product of $\psi_1(x)$ with $\psi_2(x)$ is

$$\langle\psi_1|\psi_2\rangle = \int_{-\infty}^{\infty} \psi_1^*(x)\,\psi_2(x)\,dx$$

$$= \int_{-\infty}^{\infty} AB\,x\,e^{-2x^2/a^2}\,dx = 0$$

as the integrand is an odd function of x. Hence $\psi_1(x)$ and $\psi_2(x)$ are orthogonal to each other.

7. Let $|\alpha\rangle$ and $|\beta\rangle$ represent two normalized wave functions $\alpha(x)$ and $\beta(x)$, orthogonal to each other. Let $|\psi\rangle = c_1\left[i|\alpha\rangle + 2|\beta\rangle\right]$ and $|\phi\rangle = c_2\left[|\alpha\rangle - i|\beta\rangle\right]$.

(a) Find real positive values for c_1 and c_2 so that $|\psi\rangle$ and $|\phi\rangle$ are normalized.

(b) Calculate the scalar product $\langle\psi|\phi\rangle$.

Solution: (a) $$\langle\psi|\psi\rangle = \int_{-\infty}^{\infty} c_1^*\left[-i\alpha^*(x) + 2\beta^*(x)\right]c_1\left[i\alpha(x) + 2\beta(x)\right]dx \qquad \text{(i)}$$

$$= c_1^2\left[\langle\alpha|\alpha\rangle + 2i\langle\beta|\alpha\rangle - 2i\langle\alpha|\beta\rangle + 4\langle\beta|\beta\rangle\right].$$

I have written $c_1^*c_1 = c_1^2$ because c_1 is real. Also, $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$ and $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$ as $|\alpha\rangle, |\beta\rangle$ are normalized and orthogonal to each other. Hence $\langle\psi|\psi\rangle = 5c_1^2$.

For $|\psi\rangle$ to be normalized, this should be 1. Hence $c_1 = \dfrac{1}{\sqrt{5}}$.

You need not write the integral expression explicitly as in (i) to calculate $\langle\psi|\psi\rangle$. If an expression of $|\psi\rangle$ is given in terms of other wave functions $|\alpha\rangle$, $|\beta\rangle$, ..., change these to $\langle\alpha|$, $\langle\beta|$,..... etc., and change each i to $-i$. This gives you the expression for the bra $\langle\psi|$. Use this expression to evaluate $\langle\psi|\psi\rangle$ or $\langle\psi|\phi\rangle$. I will use this method to do the rest of this problem.

$$|\phi\rangle = c_2\left[|\alpha\rangle - i|\beta\rangle\right]$$

so, $$\langle\phi| = c_2^*\left[\langle\alpha| + i\langle\beta|\right] = c_2\left[\langle\alpha| + i\langle\beta|\right].$$

Thus, $$\langle\phi|\phi\rangle = c_2\left[\langle\alpha| + i\langle\beta|\right]c_2\left[|\alpha\rangle - i|\beta\rangle\right]$$

$$= c_2^2\left[\langle\alpha|\alpha\rangle - i\langle\alpha|\beta\rangle + i\langle\beta|\alpha\rangle - i^2\langle\beta|\beta\rangle\right]$$

$$= c_2^2\left[1 - i0 + i0 + 1\right] = 2c_2^2 .$$

For $|\phi\rangle$ to be normalized, this should be equal to 1. So, $c_2 = \frac{1}{\sqrt{2}}$.

(b) $|\psi\rangle = c_1\left[i|\alpha\rangle + 2|\beta\rangle\right]$.

So, $\langle\psi| = c_1^*\left[-i\langle\alpha| + 2\langle\beta|\right] = c_1\left[-i\langle\alpha| + 2\langle\beta|\right]$.

Hence, $\langle\psi|\phi\rangle = c_1\left[-i\langle\alpha| + 2\langle\beta|\right]c_2\left[|\alpha\rangle - i|\beta\rangle\right]$

$$= c_1c_2\left[-i\langle\alpha|\alpha\rangle + i^2\langle\alpha|\beta\rangle + 2\langle\beta|\alpha\rangle - 2i\langle\beta|\beta\rangle\right]$$

$$= c_1c_2\left[-i - 2i\right]$$

$$= -3i\frac{1}{\sqrt{5}}\,\frac{1}{\sqrt{2}}$$

$$= -\frac{3i}{\sqrt{10}} .$$

8. Let $|\psi\rangle = c_1|e_1\rangle + c_2|e_2\rangle + c_3|e_3\rangle$

$|\psi'\rangle = c'_1|e_1\rangle + c'_2|e_2\rangle + c'_3|e_3\rangle$

where $|e_1\rangle$, $|e_2\rangle$, $|e_3\rangle$ are orthogonal to each other and each of these is normalized. Find $\langle\psi|\psi'\rangle$ an $\langle\psi'|\psi\rangle$.

Solution: $\langle\psi|\psi'\rangle = \left[c_1^*\langle e_1| + c_2^*\langle e_2| + c_3^*\langle e_3|\right]\left[c'_1|e_1\rangle + c'_2|e_2\rangle + c'_3|e_3\rangle\right]$

$= c_1^*c'_1\langle e_1|e_1\rangle + c_2^*c'_2\langle e_2|e_2\rangle + c_3^*c'_3\langle e_3|e_3\rangle$ (other terms are zero)

$$= c_1^*c'_1 + c_2^*c'_2 + c_3^*c'_3$$

Similarly $\langle\psi'|\psi\rangle = c'^*_1c_1 + c'^*_2c_2 + c_3^*c'_3$

In general $\langle\psi|\psi'\rangle \neq \langle\psi'|\psi\rangle$.

9. Let $\psi_1(x) = Ae^{-x^2/2}$ **and** $\psi_2(x) = Be^{-x^2}$. **Find** $\langle\psi_1|\psi_2\rangle$.

Solution: $\langle\psi_1|\psi_2\rangle = \int_{-\infty}^{\infty} A^*Be^{-\frac{x^2}{2}}\cdot e^{-x^2}dx$

$$= A^*B\int_{-\infty}^{\infty} e^{-\frac{3}{2}x^2}dx .$$

Writing $\sqrt{\frac{3}{2}}x = y,\ dx = \sqrt{\frac{2}{3}}dy$

Then $\langle\psi_1|\psi_2\rangle = A^*B\sqrt{\frac{2}{3}}\int_{-\infty}^{\infty} e^{-y^2}dy = A^*B\sqrt{\frac{2\pi}{3}}$.

$$= c_2^2\left[1 - i0 + i0 + 1\right] = 2c_2^2 .$$

For $|\phi\rangle$ to be normalized, this should be equal to 1. So, $c_2 = \frac{1}{\sqrt{2}}$.

(b) $|\psi\rangle = c_1\left[i|\alpha\rangle + 2|\beta\rangle\right]$.

So, $\langle\psi| = c_1^*\left[-i\langle\alpha| + 2\langle\beta|\right] = c_1\left[-i\langle\alpha| + 2\langle\beta|\right]$.

Hence, $\langle\psi|\phi\rangle = c_1\left[-i\langle\alpha| + 2\langle\beta|\right]c_2\left[|\alpha\rangle - i|\beta\rangle\right]$

$$= c_1c_2\left[-i\langle\alpha|\alpha\rangle + i^2\langle\alpha|\beta\rangle + 2\langle\beta|\alpha\rangle - 2i\langle\beta|\beta\rangle\right]$$

$$= c_1c_2\left[-i - 2i\right]$$

$$= -3i\frac{1}{\sqrt{5}}\,\frac{1}{\sqrt{2}}$$

$$= -\frac{3i}{\sqrt{10}}.$$

8. Let $|\psi\rangle = c_1|e_1\rangle + c_2|e_2\rangle + c_3|e_3\rangle$

$|\psi'\rangle = c'_1|e_1\rangle + c'_2|e_2\rangle + c'_3|e_3\rangle$

where $|e_1\rangle$, $|e_2\rangle$, $|e_3\rangle$ are orthogonal to each other and each of these is normalized. Find $\langle\psi|\psi'\rangle$ and $\langle\psi'|\psi\rangle$.

Solution: $\langle\psi|\psi'\rangle = \left[c_1^*\langle e_1| + c_2^*\langle e_2| + c_3^*\langle e_3|\right]\left[c'_1|e_1\rangle + c'_2|e_2\rangle + c'_3|e_3\rangle\right]$

$$= c_1^*c'_1\langle e_1|e_1\rangle + c_2^*c'_2\langle e_2|e_2\rangle + c_3^*c'_3\langle e_3|e_3\rangle \text{ (other terms are zero)}$$

$$= c_1^*c'_1 + c_2^*c'_2 + c_3^*c'_3$$

Similarly $\langle\psi'|\psi\rangle = c'^*_1c_1 + c'^*_2c_2 + c_3^*c'_3$

In general $\langle\psi|\psi'\rangle \neq \langle\psi'|\psi\rangle$.

9. Let $\psi_1(x) = Ae^{-x^2/2}$ **and** $\psi_2(x) = Be^{-x^2}$. **Find** $\langle\psi_1|\psi_2\rangle$.

Solution: $\langle\psi_1|\psi_2\rangle = \int_{-\infty}^{\infty} A^*Be^{-\frac{x^2}{2}}\cdot e^{-x^2}dx$

$$= A^*B\int_{-\infty}^{\infty} e^{-\frac{3}{2}x^2}dx.$$

Writing $\sqrt{\frac{3}{2}}x = y,\ dx = \sqrt{\frac{2}{3}}dy$

Then $\langle\psi_1|\psi_2\rangle = A^*B\sqrt{\frac{2}{3}}\int_{-\infty}^{\infty} e^{-y^2}dy = A^*B\sqrt{\frac{2\pi}{3}}$.

EXERCISES

1. Suppose the wave function of a particle at a given instant is $\psi(x) = A\cos(kx)$. Find the momentum distribution function $a(p)$. What are the possible values of momentum in this state of the particle?

Ans. $B[\delta(p-k\hbar)+\delta(p+k\hbar)]$, $-k\hbar$ and $+k\hbar$

2. Consider a particle in a state in which the linear momentum has the following distribution function

$$a(p) = \frac{1}{\sqrt{2p_0}} \qquad \text{for } -p_0 < p < p_0$$
$$= 0 \qquad \text{otherwise.}$$

(a) Check that $\int_{-\infty}^{\infty} |a(p)|^2\, dp = 1$.

(b) Find the wave function $\psi(x)$ in this state.

(c) Sketch the probability density $|\psi(x)|^2$ as a function of x.

Ans. (b) $\sqrt{\frac{p_0}{\pi\hbar}}\,\frac{\sin(p_0x/\hbar)}{(p_0x/\hbar)}$

3. The wave function of a particle at a given instant is

$$\psi(x) = \frac{1}{\sqrt{a}}\exp\left(\frac{x}{a}+\frac{i}{\hbar}p_0x\right) \qquad \text{for} \quad x \le 0$$
$$= \frac{1}{\sqrt{a}}\exp\left(-\frac{x}{a}+\frac{i}{\hbar}p_0x\right) \qquad \text{for} \quad x > 0.$$

(a) Sketch $\mathrm{Re}[\psi(x)]$ as a function of x.

(b) Find the value of b such that the probability of finding the particle in the range $-b < x < b$ is 0.9.

(c) Study the effect on $\mathrm{Re}[\psi(x)]$ as a is increased or decreased.

(d) Study the effect on $\mathrm{Re}[\psi(x)]$ as p_0 is increased or decreased.

(e) Find the momentum wave function $a(p)$ and sketch it.

(f) Study the effect on the momentum wave function as a is increased or decreased.

Ans. (b) $\approx 1.15a$ (e) $\sqrt{\frac{2\hbar^3}{\pi a^3}}\,\frac{1}{(p-p_0)^2+(\hbar/a)^2}$

4. The wave function of a particle is given as

$$\psi(x) = A(a+x) \quad \text{for} \quad -a < x \le 0$$
$$= A(a-x) \quad \text{for} \quad 0 < x < a$$
$$= 0 \quad \text{otherwise.}$$

(a) Find the value of A so that $\psi(x)$ is normalized.

(b) Sketch the wave function $\psi(x)$ and study the effect of varying a on it.

(c) Find the momentum wave function $a(p)$ and sketch it as a function of p. Study the effect of varying a on it.

Ans. (a) $\sqrt{\frac{3}{2a^3}}$ (c) $\sqrt{\frac{3a}{4\pi\hbar}}\left(\sin^2\frac{pa}{2\hbar}\right)\Big/\left(\frac{pa}{2\hbar}\right)^2$

5. The momentum wave function of a particle at a certain instant is given as

EXERCISES

1. Suppose the wave function of a particle at a given instant is $\psi(x) = A\cos(kx)$. Find the momentum distribution function $a(p)$. What are the possible values of momentum in this state of the particle?

Ans. $B\left[\delta(p - k\hbar) + \delta(p + k\hbar)\right], -k\hbar$ and $+k\hbar$

2. Consider a particle in a state in which the linear momentum has the following distribution function

$$\begin{aligned} a(p) &= \frac{1}{\sqrt{2p_0}} \qquad \text{for } -p_0 < p < p_0 \\ &= 0 \qquad \text{otherwise.} \end{aligned}$$

(a) Check that $\int_{-\infty}^{\infty} |a(p)|^2\, dp = 1$.

(b) Find the wave function $\psi(x)$ in this state.

(c) Sketch the probability density $|\psi(x)|^2$ as a function of x.

Ans. (b) $\sqrt{\frac{p_0}{\pi\hbar}}\,\frac{\sin(p_0 x/\hbar)}{(p_0 x/\hbar)}$

3. The wave function of a particle at a given instant is

$$\begin{aligned} \psi(x) &= \frac{1}{\sqrt{a}}\exp\left(\frac{x}{a} + \frac{i}{\hbar}p_0 x\right) \qquad \text{for} \quad x \le 0 \\ &= \frac{1}{\sqrt{a}}\exp\left(-\frac{x}{a} + \frac{i}{\hbar}p_0 x\right) \qquad \text{for} \quad x > 0. \end{aligned}$$

(a) Sketch $\text{Re}[\psi(x)]$ as a function of x.

(b) Find the value of b such that the probability of finding the particle in the range $-b < x < b$ is 0.9.

(c) Study the effect on $\text{Re}[\psi(x)]$ as a is increased or decreased.

(d) Study the effect on $\text{Re}[\psi(x)]$ as p_0 is increased or decreased.

(e) Find the momentum wave function $a(p)$ and sketch it.

(f) Study the effect on the momentum wave function as a is increased or decreased.

Ans. (b) $\approx 1.15a$ (e) $\sqrt{\frac{2\hbar^3}{\pi a^3}}\,\frac{1}{(p - p_0)^2 + (\hbar/a)^2}$

4. The wave function of a particle is given as

$$\begin{aligned} \psi(x) &= A(a + x) \quad \text{for} \quad -a < x \le 0 \\ &= A(a - x) \quad \text{for} \quad 0 < x < a \\ &= 0 \qquad \text{otherwise.} \end{aligned}$$

(a) Find the value of A so that $\psi(x)$ is normalized.

(b) Sketch the wave function $\psi(x)$ and study the effect of varying a on it.

(c) Find the momentum wave function $a(p)$ and sketch it as a function of p. Study the effect of varying a on it.

Ans. (a) $\sqrt{\frac{3}{2a^3}}$ (c) $\sqrt{\frac{3a}{4\pi\hbar}}\left(\sin^2\frac{pa}{2\hbar}\right)\Big/\left(\frac{pa}{2\hbar}\right)^2$

5. The momentum wave function of a particle at a certain instant is given as

$$a(p) = \sqrt{\frac{3}{2d^3}}\,(d + p - p_0) \quad \text{for } p_0 - d < p \le p_0$$
$$= \sqrt{\frac{3}{2d^3}}\,(d - p + p_0) \quad \text{for } p_0 < p < p_0 + d$$
$$= 0 \quad \text{otherwise.}$$

Here p_0 and d are constants. (a) Sketch $a(p)$. (b) Find the probability of finding the momentum less than p_0. (c) Find the wave function $\psi(x)$. Sketch $\text{Re}[\psi(x)]$ as a function of x. (d) Study the effect on Re $\psi(x)$ as d is changed. (e) Study the effect on Re $\psi(x)$ as p_0 is changed.

Ans. (b) 0.5 (c) $\sqrt{\frac{3d}{4\pi\hbar}}\,\frac{\sin^2\alpha}{\alpha^2}\,e^{\frac{i}{\hbar}p_0x}$ where $\alpha = \frac{xd}{2\hbar}$

6. The wave function of a particle is given by $\psi(x) = f(x)e^{ik_0x}$ where

$$f(x) = \frac{A}{\epsilon}x \quad \text{for } 0 < x \le \epsilon$$
$$= A \quad \text{for } \epsilon < x \le a$$
$$= A\left[1 + \frac{a - x}{\epsilon}\right] \quad \text{for } a < x \le a + \epsilon$$
$$= 0 \quad \text{otherwise}$$

For parts (b) to (d) assume that $\epsilon \to 0$.

(a) Sketch $f(x)$ as a function of x. Show that it is continuous and finite everywhere.

(b) Find the value of A for which $\psi(x)$ is normalized.

(c) Find the momentum probability density $|a(p)|^2$ for this wave function.

(d) At which value of momentum is $|a(p)|^2$ maximum? What is the value of this maximum?

Ans. **(b)** $1/\sqrt{a}$ **(c)** $\frac{2\sin^2\left[\left(k_0 - \frac{p}{\hbar}\right)\frac{a}{2}\right]}{\pi\hbar a\left(k_0 - p/\hbar\right)^2}$, **(d)** $\hbar k_0, \frac{a}{2\pi\hbar}$

7. Suppose the momentum wave function of a particle is $a(p) = Ae^{-p^2/\lambda^2}$. Find the wave function of the particle.

Ans. $\frac{A\lambda}{\sqrt{2\hbar}}e^{-\frac{x^2\lambda^2}{4\hbar^2}}$

8. Find the scalar product $\langle x_0|p_0\rangle$ where $|x_0\rangle = \delta(x - x_0)$ and $|p_0\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}p_0x}$. **Ans.** $\frac{1}{2\pi\hbar}e^{\frac{i}{\hbar}p_0x_0}$

9. Find the scalar product $\langle p_1|p_2\rangle$ where $|p_1\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}p_1x}$ and $|p_2\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}p_2x}$. **Ans.** $\delta(p_1 - p_2)$

10. Let $|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$ represent three normalized wave functions orthogonal to each other. Also let

$$|\psi\rangle = c_1\big[|\alpha\rangle + 2|\beta\rangle + (1+i)|\gamma\rangle\big] \text{ and } |\phi\rangle = c_2\big[|\alpha\rangle - i|\beta\rangle + |\gamma\rangle\big].$$

(a) Find real, positive values of c_1 and c_2 for which $|\psi\rangle$ and $|\phi\rangle$ are normalized. (b) Calculate $\langle\psi|\phi\rangle$.

Ans. (a) $\frac{1}{\sqrt{7}}, \frac{1}{\sqrt{3}}$ (b) $\frac{2-3i}{\sqrt{21}}$

11. Find the scalar product of $\psi_1(x) = Ae^{-x^2/2}$ and $\psi_2(x) = Be^{-x^2} + Ce^{-x^2/2}$ **Ans.** $A^*\sqrt{\pi}\left(B\sqrt{\frac{2}{3}}+C\right)$

12. Let $\psi_1(x) = \frac{2}{\sqrt{L}}\sin\frac{3\pi x}{2L}\cos\frac{\pi x}{2L}$ for $0 < x < L$

$= 0$ otherwise.

$\psi_2(x) = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}$ for $0 < x < L$

$= 0$ otherwise.

Find the scalar product $\langle\psi_1|\psi_2\rangle$. **Ans.** $\frac{1}{\sqrt{2}}$

5

A Restriction on Experimentalists—Heisenberg Uncertainty Principle

5.1 Position and momentum uncertainty

To find the position and velocity of a particle at a given time when the initial position and velocity are given and forces are known, is a common variety of high school physics problems. You use equations like

$$x = ut + \frac{1}{2}at^2$$

and come up with an answer like $x = 12$ m and $v = 8$ m/s and so on. This is good as long as our particle is big—a piece of stone, a steel ball, an wooden block, a dust particle, etc. But for a quantum system like a molecule, an atom, an electron, etc., saying that $x = 12$ m, will invite lots of criticism. A particle cannot be at a particular point (as suggested by $x = 12$ m) at any given time. If it is, its wave function will be a Dirac delta function centered at that point and this is unrealistic. At any time the wave function of the particle has some spread making the position uncertain in a range. If the wave function is spread in the range x_1 to x_2, the position can be anything between x_1 and x_2. We say that position has an uncertainty of roughly $\Delta x \approx |x_2 - x_1|$. In any realistic situation, the particle has some position uncertainty Δx.

Similar is the case with linear momentum. Telling an exact value of velocity and hence the momentum is not allowed for a quantum system. At any given time, the momentum of a particle cannot have a precisely defined single value p. If it is so, its wave function will be a plane wave which is not a realistic wave function. The linear momentum of a particle at any time is spread over a range p_1 to p_2. We say that the momentum has an uncertainty of roughly $\Delta p_x \approx |p_2 - p_1|$. As the momentum we are talking about is in x-direction, I have used the symbol Δp_x for its uncertainty with x as the subscript.

It turns out that for any wave function, that is, for any state of the particle, Δx and Δp_x both cannot be made very small. If you choose a wave function in which Δx is very small, Δp_x will be quite large. And if you choose a wave function in which Δp_x is very small, Δx will be quite large. Let me give you a feel of this fact by considering the extreme cases, one in which $\Delta x = 0$ and the other in which $\Delta p_x = 0$.

Case I: $\Delta x = 0$

The position uncertainty Δx is zero only if the position of the particle is precisely known. This means, the wave function of the particle is

$$\psi(x) = A\,\delta(x - x_0).$$

What can you say about its momentum? You know that it is not a plane wave, so it does not have a unique value of momentum. What is the probability that a momentum measurement will give a value between p and $p + dp$? You know how to get it. It is $|a(p)|^2\,dp$ where $a(p)$ is obtained from $\psi(x)$ using the equation

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x) e^{-\frac{i}{\hbar}px} dx.$$

Using $\psi(x) = A\,\delta(x - x_0)$,

$$a(p) = \frac{A}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-\frac{i}{\hbar}px} \delta(x - x_0)\, dx = \frac{A}{\sqrt{2\pi\hbar}} e^{-\frac{i}{\hbar}px_0}.$$

I have used the property $\int_{-\infty}^{\infty} f(x)\delta(x - x_0)dx = f(x_0)$ of delta functions to evaluate the integration.

Thus,

$$|a(p)|^2\, dp = \frac{|A|^2}{2\pi\hbar} \left| e^{-\frac{i}{\hbar}px_0} \right|^2 dp$$

$$= \frac{|A|^2}{2\pi\hbar} e^{-\frac{i}{\hbar}px_0} e^{\frac{i}{\hbar}px_0} dp = \frac{|A|^2}{2\pi\hbar} dp.$$

This is independent of p. Thus all values of p from $-\infty$ to $+\infty$ are equally likely. The momentum is completely uncertain. Hence, the uncertainty in momentum is $\Delta p_x = \infty$.

If you take a wave function with $\Delta x = 0$, then Δp_x will be ∞.

Case II: $\Delta p_x = 0$

If the momentum of a particle is precisely known at an instance, i.e., $\Delta p_x = 0$, its wave function at that instant must be a plane wave

$$\psi(x) = \frac{A}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}px}.$$

What is the position of the particle? If a position measurement is made when the particle is described by the above wave function, the probability of getting a value between x and $x + dx$ is given by

$$|\psi(x)|^2\, dx = \frac{|A|^2}{2\pi\hbar} \left| e^{\frac{i}{\hbar}px} \right|^2 dx = \frac{|A|^2}{2\pi\hbar} dx.$$

So, what do you find? The probability is independent of x. All values of x from $-\infty$ to $+\infty$ are equally likely. The position is completely uncertain. The uncertainty in position is $\Delta x = \infty$.

5.2 Exact definition of Δx and Δp_x

I showed you in Section 5.1 that a wave function that allows precise determination of position ($\Delta x = 0$) is completely uncertain about the momentum and the one which allows a precise determination of momentum ($\Delta p_x = 0$) is completely uncertain about the position. Both of these are hypothetical situations as in any realistic case we have neither $\Delta x = 0$ nor $\Delta p_x = 0$. However, the inverse relationship between the uncertainties in position and momentum holds in case of real situations too and can be put in terms of a mathematical inequality. But before telling you about this inequality, I will first define these uncertainties in a more formal way.

Consider the marks $M_1, M_2, M_3, \ldots, M_N$ of N students in a certain examination. A statistician will be interested in knowing the average marks and also the spread in the marks. The average is obtained by the formula that you learned in your childhood

$$\overline{M} = \langle M \rangle = \frac{M_1 + M_2 + M_3 + \dots + M_N}{N} = \frac{1}{N}\sum_{i=1}^{N} M_i .$$

$\overline{M}$ and $\langle M \rangle$ are two common symbols used to denote the average. The spread in the marks is measured by a quantity called *standard deviation* σ, defined as

$$\sigma = \sqrt{\frac{1}{N}\sum_i \left(M_i - \overline{M}\right)^2} . \tag{5.1}$$

You can understand why this quantity represents the spread in *M*. Suppose there is no spread, that is, all the students get the same marks *M*. The mean $\overline{M}$ will also be *M*. Then $M_i = \overline{M}$ for each *i* and $\sigma = 0$. If marks deviate from the average, $\left(M_i - \overline{M}\right)^2$ gives the idea of deviation from the mean, this side or that side. Equation 5.1 takes the contributions from all values M_i and averages it. Hence, it is a measure of the spread in the quantity *M*. Equation 5.1 is equivalent to

$$\sigma = \left[\frac{1}{N}\sum M_i^2 - \left(\frac{1}{N}\sum M_i\right)^2\right]^{1/2} = \left[\langle M^2 \rangle - \langle M \rangle^2\right]^{1/2} . \tag{5.2}$$

Next, consider a LUDO dice. It is a small solid cube and different number of dots, varying between 1 and 6, are painted on its six faces. When you throw the dice, the number of dots on the top face is the number you play with.

Suppose you throw the dice a large number of times and note down the numbers x_1, x_2, x_3,..., x_N you get on the top face. If the dice is well made each of the six numbers will be equally likely. So 1 will occur close to $N/6$ times, 2 will also occur close to $N/6$ times, and so on. We say that the probability of each number is $p_i = 1/6$. What is the average of these numbers? It is,

$$\begin{aligned} \langle x \rangle &= \frac{1}{N}\sum_{i=1}^{N} x_i \\ &= \frac{1}{N}\left[1 \times \frac{N}{6} + 2 \times \frac{N}{6} + 3 \times \frac{N}{6} + 4 \times \frac{N}{6} + 5 \times \frac{N}{6} + 6 \times \frac{N}{6}\right] \\ &= \frac{21}{6} = 3.5. \end{aligned}$$

And what is the standard deviation? It is represented by

$$\sigma = \left[\langle x^2 \rangle - \langle x \rangle^2\right]^{1/2},$$

$$\begin{aligned} \langle x^2 \rangle &= \frac{1}{N}\sum x_i^2 \\ &= \frac{1}{N}\left[1^2 \times \frac{N}{6} + 2^2 \times \frac{N}{6} + 3^2 \times \frac{N}{6} + 4^2 \times \frac{N}{6} + 5^2 \times \frac{N}{6} + 6^2 \times \frac{N}{6}\right] = 91/6 . \end{aligned}$$

So, $$\sigma = \left[(91/6) - (3.5)^2\right]^{1/2} \approx 1.7 .$$

Now just imagine, the dice is in your hand and you are about to throw it. Are you certain what is going to be the number on the top? You are not. If you get 5 or 6 perhaps you think great. If you get 1 or 2 you say ooonh! Only this much. If it is 3 or 4 you say OK, what else one can expect in general. In fact the average 3.5 of a large number of throws is also your expectation in a single throw. In probability theory, the average of a large number of occurrences of a variable is called its *expectation value*.

How much is the uncertainty? Roughly speaking, anything between 1 and 6 is possible and the expectation value is 3.5, so uncertainty is ± 2.5. But we need a more precise definition of uncertainty. Mathematicians and physicists agree to use the standard deviation σ as a measure of uncertainty. After all, uncertainty is because of the spread in the various possible values of x, and σ measures the spread. So, the uncertainty Δx in x is defined by

$$\Delta x = \left[\left\langle x^2\right\rangle - \langle x\rangle^2\right]^{1/2}. \tag{5.3}$$

For the unbiased LUDO dice, the expectation value is 3.5 and the uncertainty is 1.7 as calculated above.

Next suppose a variable x can take values x_1, x_2, x_3,...., with probabilities p_1, p_2, p_3... If we pick up a large number N of the values of x, x_1 will occur Np_1 times, x_2 will occur Np_2 times, and so on. So,

$$\langle x\rangle = \frac{1}{N}\sum_{i=1}^{N} x_i = \frac{1}{N}\left[x_1 \times Np_1 + x_2 \times Np_2 + ...\right] = \sum_i x_i p_i \tag{5.4}$$

and

$$\left\langle x^2\right\rangle = \frac{1}{N}\sum_{i=1}^{N} x_i^2 = \frac{1}{N}\left[x_1^2 \times Np_1 + x_2^2 \times Np_2 + ...\right] = \sum_i x_i^2 p_i . \tag{5.5}$$

In fact, for any function of x say $f(x)$, the expectation value is

$$\langle f(x)\rangle = \sum_i f(x_i) p_i . \tag{5.6}$$

Now consider a particle with wave function $\psi(x)$. Consider the variable x representing its position in an ideal position measurement. Beforehand I do not know what value will be obtained in the measurement. It can be anything from $x = -\infty$ to $+\infty$. I wish to know the expectation value and the uncertainty in x. Can I use Equations 5.3 to 5.5 for this purpose? There is a difference because here x (position) is a continuous variable. I do not have the probability for a particular value $x = x_i$ but I have the probability for a particular range x to $x + dx$. I can still use the above equations but with slight modification. The summation $i = 1$ to N will be replaced by integration from $x = -\infty$ to ∞ and the probability p_i for the value x_i will be replaced by dP for the range x to $x + dx$.

The expectation value of position is $\langle x\rangle = \int_{x=-\infty}^{\infty} x\, dP$. But the probability dP for finding the particle in the range x to $x + dx$ is equal to $dP = |\psi(x)|^2\, dx$. So,

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi(x)|^2\, dx . \tag{5.7}$$

Similarly

$$\begin{aligned}\left\langle x^2\right\rangle &= \int_{x=-\infty}^{\infty} x^2\, dP \\ &= \int_{-\infty}^{\infty} x^2 |\psi(x)|^2\, dx .\end{aligned} \tag{5.8}$$

In fact, for any function of x, say $f(x)$, the expectation value is

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)|\psi(x)|^2 dx . \tag{5.9}$$

The uncertainty in the position of the particle, for which the wave function is $\psi(x)$, is, as usual,

$$\Delta x = \left[\left\langle x^2\right\rangle - \langle x\rangle^2\right]^{1/2}$$

where $\langle x\rangle$ and $\left\langle x^2\right\rangle$ are given by Equations 5.7 and 5.8 respectively.

This gives the uncertainty in position. Next consider momentum. The particle has wave function $\psi(x)$. What will be the momentum (x-component) obtained if an ideal momentum measurement is made on this system? It can be anything from $-\infty$ to $+\infty$. The probability that the value is between p and $p + dp$ is $|a(p)|^2\, dp$ where $a(p)$ is obtained from $\psi(x)$ by the usual Fourier transformation equation. The expectation values of p and p^2 are

$$\langle p_x\rangle = \int_{-\infty}^{\infty} p\, |a(p)|^2\, dp$$

and

$$\left\langle p_x^2\right\rangle = \int_{-\infty}^{\infty} p^2\, |a(p)|^2\, dp$$

and the uncertainty in momentum is

$$\Delta p_x = \left[\left\langle p_x^2\right\rangle - \langle p_x\rangle^2\right]^{1/2}. \tag{5.10}$$

Again I am using the subscript x to remind that we are working only with x-component of momentum.

5.3 Heisenberg uncertainty principle

With uncertainties in position and momentum as defined above, it turns out that you take any wave function $\psi(x)$ representing a state of a particle, and you will have,

$$\Delta x\, \Delta p_x \geq \hbar/2. \tag{5.11}$$

This relation is called *Heisenberg uncertainty principle*. It can be proved using the properties of Fourier transformation. However, I am not interested in working out all that mathematics, because the physical implications of the uncertainty principle are much more interesting to discuss.

Heisenberg uncertainty principle puts a theoretical restriction on our capability of accurately measuring certain quantities. If I need to know the position of a particle I make a position measurement by doing an appropriate experiment. Now I am talking of real experiment in the laboratory and not an ideal experiment. It may be X-ray diffraction, scattering of light from the particle, interaction with photographic plate or whatever else I can think of. When I do the experiment, I get the position of the particle with an uncertainty Δx. How small or how large is Δx? That depends on my experimental set up and my ability to perform the experiment. Heisenberg uncertainty principle puts no theoretical restriction on it. It could be an angstrom or one-tenth of an angstrom or a femtometer, depending on how advanced is my technology. However, the measurement will leave the particle in a new state. Remember, measurement disturbs the system. Before the measurement, the particle was in a state say $|\phi_1\rangle$, after the measurement the state becomes $|\phi_2\rangle$. It is in this state $|\phi_2\rangle$ that we know the position with an uncertainty Δx. The uncertainty principle says that in this state $|\phi_2\rangle$ the momentum uncertainty cannot be less than $\hbar/(2\Delta x)$. My measuring device which gives the position with an uncertainty Δx, must have changed its state in such a way that the momentum uncertainty is at least $\hbar/(2\Delta x)$ now. The theory says that no experiment can ever be designed which measures the position with an accuracy better than Δx and leaves the system in a state in which the momentum has an uncertainty less than $\hbar/(2\Delta x)$.

Similarly, I can design an experiment which measures the momentum with an uncertainty Δp_x as small as I wish. If I am not able to achieve the accuracy I wish, it is because I am not using sufficiently advanced technology or I have not designed my experiment well. There is no theoretical restriction on how small Δp_x I can achieve. But whatever experiment I do, if I know the momentum with an uncertainty Δp_x, I must have disturbed the system and left it in a state with position uncertainty Δx which is at least $\hbar/(2\Delta p_x)$. You cannot create a state of the particle in which position uncertainty Δx momentum uncertainty (in the same state) is Δp_x and $\Delta x\ \Delta p_x$ is less than $\hbar/2$.

So the theory has thrown a challenge to the experimentalists. The challenge is still open. Any day if someone comes up with an experiment which defies uncertainty principle she/he will bring a revolution in science.

5.4 Experiments which tried to beat uncertainty principle but failed

In the formative periods of quantum mechanics, uncertainty principle was very difficult for physicists to accept. It is said that Einstein was never comfortable with this principle. People thought of different experiments which would *in principle* be doable but which would defy uncertainty principle. I will describe two of them. In each of these, a beam of electrons is produced (remember these are only thought experiments and are not done in a laboratory) with well defined momentum and an attempt is made to locate an electron in this beam to an arbitrary precision.

(a) Locate by passing through a slit : diffraction experiment

Suppose electrons of a given kinetic energy E are coming from a source such as a hot filament placed away from us. In order to get an electron with known position, we put a metallic plate which has a hole of diameter b in it. Take the center of the hole as the origin and x-axis along a diameter of the hole. The y-direction is taken perpendicular to the plate. An electron that comes out of the hole, must be somewhere in front of the hole. Thus the uncertainty in the position (x) of this electron at this instant is of the order of the diameter b of the hole. By decreasing the diameter of the hole, I can reduce this uncertainty Δx.

However, it is also an experimental fact that electrons diffract from the hole and change their direction of motion. Electron diffraction is similar to that of any other wave and follows the same rule. Most of the electrons that pass through the hole go in a cone of semivertical angle θ_m where

$$\sin\theta_m = \frac{1.22\lambda}{b} \approx \frac{\lambda}{b} \qquad \text{(i)}$$

where λ is the de Broglie wavelength. The particular electron that we are talking of and for which $\Delta x \approx b$, may be diffracted in any direction given by θ which is roughly confined to the range $-\theta_m$ to θ_m. The magnitude of the momentum p is related to the de Broglie wavelength as $p = h/\lambda$ and the x-component of the momentum is

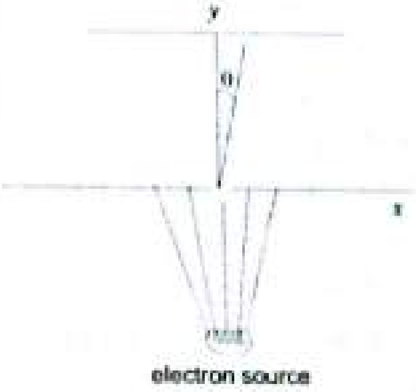


Fig. 5.1

$$p_x = p\sin\theta = \frac{h}{\lambda}\sin\theta. \qquad \text{(ii)}$$

As θ is distributed in the range $-\theta_m$ to θ_m, we do not know p_x precisely without actually measuring the direction of motion of the electron after it came out of the hole. As $\sin\theta$ varies from say $-\sin\theta_m$ to $+\sin\theta_m$, p_x varies from $-\frac{h}{\lambda}\sin\theta_m$ to $\frac{h}{\lambda}\sin\theta_m$. Thus, the uncertainty in p_x is, from (i) and (ii)

$$\Delta p_x \approx \frac{h}{\lambda}\sin\theta_m = \frac{h}{\lambda}\times\frac{\lambda}{b} = \frac{h}{b}.$$

So if I reduce the width b of the hole, the uncertainty Δx is reduced, but Δp_x is increased. On the other hand if I take a plate with a bigger hole, Δp_x will be small, but that will increase Δx. So it is not possible, by this arrangement, to produce an electron which has both Δx and Δp_x very small. The uncertainty product in this case is, $\Delta x \, \Delta p_x = (b) \times (h/b) = h$, consistent with the uncertainty principle.

Indeed we have not used the precise definition of Δx and Δp_x. But the idea is to get the feel of the Nature's meticulous consistency. Make the hole smaller and the angular divergence of the beam increases. Getting information about position is accompanied by the loss of momentum information and vice versa.

What if I make an accurate measurement of momentum after making an accurate position measurement? Will that give me a very small Δx and also a very small Δp_x ? No, it will not. When I do the momentum measurement, it will disturb the system and the information about the position obtained in the first experiment will be lost resulting in larger position uncertainty.

(b) Locate by illuminating with light: Heisenberg's gamma-ray microscope

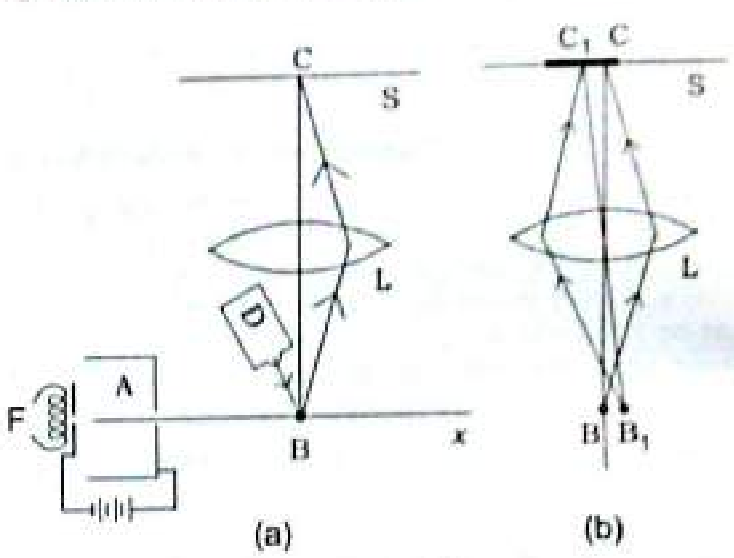


Fig. 5.2

Consider the experimental arrangement shown in Figure 5.2a. If I heat the filament F, it will emit electrons with small starting velocity. The arrangement A is to serve two purposes. The electrons are allowed to go beyond A only through the slits and hence it aligns the electron beam in the direction of the x-axis (towards right in Figure 5.2a). The slits are wide but are at sufficiently large separation to ensure that any electron going beyond A, has a linear momentum almost in the x-direction. Another purpose is to create an electric field that accelerates the electrons in the x-direction. If the potential difference through which the electron travels is V, the kinetic energy acquired is $p_x^2/2m = eV$. Thus the linear momentum $p_x = \sqrt{2meV}$. Thus I know the linear momentum p_x with a very good accuracy and Δp_x is very small.

However, as any given electron can be anywhere in the beam (along the x-axis), I have no knowledge about its position x. The uncertainty Δx is very large.

To acquire knowledge about the position of an electron, I have put a light source D, a lens L and a screen S. On the screen I have put some chemical at point C, so that if a photon of light hits this point I come to know that it has done so. BC is the principal axis of the lens. The distances are so adjusted that light starting from B should reach the screen at C according to the lens equation $\frac{1}{v} - \frac{1}{u} = \frac{1}{f}$. If the object point is to the right of B, light will reach the screen to the left of C (Figure 5.2b) and if the object point is to the left of B, light will reach the screen to the right of C.

The idea is the following. As I switch on the light source D, some photon emitted by D will fall on the electron at B. This photon will scatter from the electron and may go through the lens. If it does not do so, some other photon will do so. If the photon, scattered from the electron at B, goes through the lens, it will hit the screen at C. The moment I find a photon hitting at C (the chemical changes at C will tell me that), I know that there was an electron at B. So now I have located the electron to be at B and so Δx is negligibly small or zero.

Δp_x was already negligibility small and now Δx is also negligibly small and hence I seem to have defied Heisenberg uncertainty principle $\Delta x \, \Delta p_x \geq \hbar/2$.

Where have I ditched you in the above arguments? I have not considered the diffraction effects when an image is formed by a lens. When an image of a point object B is formed by a lens of radius R, the image is not a point image, but it spreads to form a nearly disk type image. If λ is the wavelength of the light used, the radius of the image disk forms an angle θ at the centre of the lens, is given by

$$\theta \approx \frac{\lambda}{2R}. \qquad \text{(i)}$$

So the photon may land up at a position other than that predicted by the lens formula and the deviation is governed by equation (i).

This means, if my light source D sends a photon to the electron at B and the photon after hitting the electron goes through the lens, it may not strike the screen at C. This is not too bad. The diffraction equation does not tell that your photon will always miss C. In fact the probability of its striking C is still reasonably high. But worse part is that a photon which is scattered by an electron not at B, can also strike the screen at C. Suppose the photon starts from B_1 (Figure 5.2b). According to the geometrical optics the photon should strike the screen at C_1. But due to diffraction, the image is like a disk centered at C_1 with a radius r. I have shown this disk by the thick line in Figure 5.2b. The photon coming from B_1 can strike anywhere in the disk image. If B_1 is sufficiently close to B, the disk will include the point C and hence the photon starting from B_1 can reach C. This means even if you find that a photon has struck at C, you are not sure that it is coming from the electron at B. The uncertainty Δx is not really negligibly small. Let me estimate Δx.

In Figure 5.3a, I show the range B_1B_2 from where the photon can reach the point C taking account of diffraction effects. The disk image of B_1 is centered at C_1 and just includes C. Similarly, the disk image of B_2 is centered at C_2 and just includes C. So, $C_1C = C_2C = r$. Each of these makes the same angle θ at the center of the lens. B_1B_2 makes the same angle 2θ at the centre of the lens as made by C_1C_2. If d be the distance of the point B from the centre of the lens to the point B,

$$B_1B_2 \approx (2\theta)d = \frac{\lambda d}{R}.$$

So, the position uncertainty is

$$\Delta x = \frac{\lambda d}{R}. \qquad \text{(ii)}$$

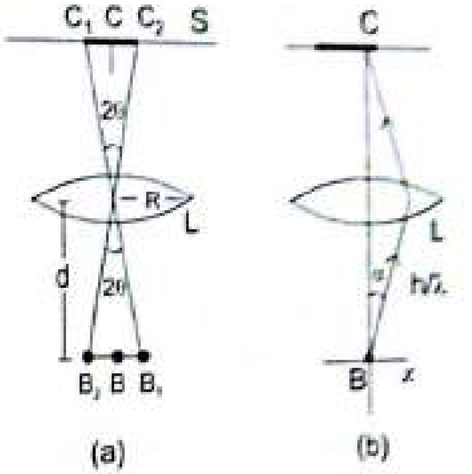


Fig. 5.3

OK. But that should not be too bad. I can choose a small λ (perhaps by using gamma rays) or large R and make Δx again negligibly small. I already had Δp_x negligibly small and so I still have a chance to make $\Delta x\, \Delta p_x$ smaller than $\hbar/2$. But not really so. I had Δp_x of the electron negligibly small *before the photon scattered from it.* I am sending the photon from D which has a well defined momentum $\mathbf{p}_1$. Before the scattering, the electron also had a well defined momentum $\mathbf{p}_2$. So, before the scattering, the momentum of the photon-electron system is $\mathbf{p}_1 + \mathbf{p}_2$. After the scattering also the total momentum is $\mathbf{p}_1 + \mathbf{p}_2$. But the photon reaching C can come from any part of the lens. The momentum of the photon is h/λ. If it starts from B at an angle α from BC (Figure 5.3b), the x-component of its momentum will be $\frac{h}{\lambda}\sin\alpha$. Now $\sin\alpha$ can be anything from zero to R/d (Assume R << d). So the x-component of momentum of the photon is uncertain by

$$\Delta p'_x = \frac{h}{\lambda} \times \frac{R}{d}$$

As the total momentum of the electron and the photon is definite, the electron momentum should also become uncertain by this same amount. Actually, when the photon hits the electron, it changes the path of the electron a little. This changes the x-component of the momentum of the electron and introduces uncertainty in it. The uncertainty is

$$|\Delta p_x| = |\Delta p_x'| = \frac{hR}{\lambda d}. \qquad \text{(iii)}$$

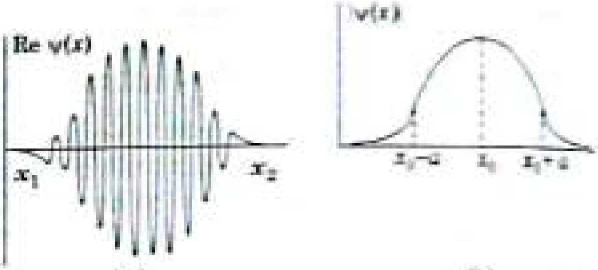
Using (ii) and (iii),

$$\Delta x\,\Delta p_x = \frac{\lambda d}{R} \times \frac{hR}{\lambda d} = h.$$

This is independent of λ and R. You cannot reduce the uncertainty product arbitrarily by choosing λ and/or R.

The arrangement described in this section is called Heisenberg's gamma ray microscope.

5.5 The best I can do—Gaussian wave packet



(a) (b)

Fig. 5.4

Suppose the wave function of a particle at a given instant is,

$$\psi(x) = \left(\frac{2}{\pi a^2}\right)^{1/4} e^{-(x-x_0)^2/a^2} e^{\frac{i}{\hbar}p_0 x}. \qquad (5.12)$$

You cannot plot it because of the imaginary number i involved. But if you plot the real part or the imaginary part as a function of x, the shape will be as shown in Figure 5.4a. It is a wave packet confined in a finite range. The absolute value is maximum at $x = x_0$ and decreases as one goes away from this point as shown in Figure 5.4b. At $x = x_0 \pm a$, it is decreased by a factor of $1/e$, i.e., to about 37% of the maximum. Though $|\psi(x)|$ does not become zero at any finite value of x, it becomes very small as one moves a distance few times of "a" on either side of x_0.

The factor $\left(\frac{2}{\pi a^2}\right)^{1/4}$ appearing in Equation 5.12 ensures that the wave function is normalized.

The probability density for position is

$$\begin{aligned} |\psi(x)|^2 &= \psi^*(x)\,\psi(x) \\ &= \left(\frac{2}{\pi a^2}\right)^{1/2} e^{-2(x-x_0)^2/a^2}\, e^{-\frac{i}{\hbar}p_0 x}\, e^{\frac{i}{\hbar}p_0 x} \\ &= \left(\frac{2}{\pi a^2}\right)^{1/2} e^{-2(x-x_0)^2/a^2}. \end{aligned} \qquad \text{(i)}$$

Mathematicians call the above function in (i) a *Gaussian function*. The wave packet $\psi(x)$ described in Equation 5.12 is therefore called a *Gaussian wave packet*. Any function $\psi(x)$ can be written in the form $\psi(x) = |\psi(x)| e^{i\phi(x)}$ where $\phi(x)$ is a real function. We call a wave function $\psi(x)$ a Gaussian wave packet if

(a) $|\psi(x)|$ is a Gaussian function

(b) $\phi(x)$ is linear in x, such as $\frac{p_0}{\hbar}x$.

The factor $e^{-(x-x_0)^2/a^2}$ in Equation 5.12 ensures the first condition. The part $e^{\frac{i}{\hbar}p_0x}$ gives it an oscillatory character and satisfies the second condition. If $e^{-(x-x_0)^2/a^2}$ term were not there in Equation 5.12 it would be a plane wave with a definite linear momentum p_0 and wavelength h/p_0. But because of the factor $e^{-(x-x_0)^2/a^2}$, it is no more a plane wave and hence does not allow a single wavelength and a single momentum.

Let me now calculate Δx and Δp_x for the particle with the wave function given by Equation 5.12.

$$\langle x\rangle = \int_{-\infty}^{\infty} x|\psi(x)|^2\,dx$$

$$= \int_{-\infty}^{\infty} x\left(\frac{2}{\pi a^2}\right)^{1/2} e^{-2(x-x_0)^2/a^2}\,dx = x_0. \qquad \text{(ii)}$$

This is expected because the function $|\psi(x)|$ (plotted in Figure 5.4b) and hence $|\psi(x)|^2$ is symmetric on both sides about the point $x = x_0$.

$$\langle x^2\rangle = \int_{-\infty}^{\infty} x^2\,|\psi(x)|^2\,dx$$

$$= \int_{-\infty}^{\infty} x^2\left(\frac{2}{\pi a^2}\right)^{1/2} e^{-2(x-x_0)^2/a^2}\,dx = \frac{a^2}{4} + x_0^2.$$

The uncertainty in x is

$$\Delta x = \left[\langle x^2\rangle - \langle x\rangle^2\right]^{1/2} = \frac{a}{2}. \qquad \text{(iii)}$$

To calculate Δp_x, we find $a(p)$.

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\psi(x)e^{-\frac{i}{\hbar}px}\,dx$$

$$= \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\left(\frac{2}{\pi a^2}\right)^{1/4} e^{-\frac{(x-x_0)^2}{a^2}+\frac{i}{\hbar}p_0x-\frac{i}{\hbar}px}\,dx$$

$$= B\,e^{-\frac{a^2(p-p_0)^2}{4\hbar^2}}$$

where B is a constant. The momentum probability density is

$$|a(p)|^2 = |B|^2\,e^{-\frac{a^2(p-p_0)^2}{2\hbar^2}} = B^2 e^{-\frac{2(p-p_0)^2}{(2\hbar/a)^2}}.$$

This itself is a Gaussian function in p centered at p_0 as can be seen by comparing it with equation (i). The results for $\langle p_x\rangle$ and Δp_x can be written by comparison with (ii) and (iii). The average value or the expectation value of the momentum is

$$\langle p_x\rangle = p_0$$

and the uncertainty in momentum is

$$\Delta p_x = \frac{(2\hbar)}{a} \times \frac{1}{2} = \frac{\hbar}{a}.$$

The uncertainty product is

$$\Delta x\, \Delta p_x = \left(\frac{a}{2}\right) \times \frac{\hbar}{a} = \frac{\hbar}{2}.$$

Thus the Gaussian wave packet corresponds to the state of the particle in which the uncertainty product $\Delta x\, \Delta p_x$ has its minimum possible values, i.e., $\hbar/2$.

5.6 Can I continue to use classical physics for my kancha?

The new rules of game that I am describing in the name of quantum mechanics tell that, in general, you should not say that at this time the position x of the particle under consideration is this much unless you have actually measured it. Similarly don't say that the momentum p is this much at this time. And in no case try to give precise values of x and p at the same time.

But people still use Newton's laws. We use "initial conditions" where the values of x and p are precisely given at the same time $t = 0$. The purpose of solving Newton's laws is to find the precise values of x and p at some general instant of time t, a concept totally rejected by Heisenberg uncertainty principle.

We have not stopped teaching Newton's laws after the invention of quantum mechanics. These laws are still used successfully in all calculations of spacecraft projections and a spacecraft sent to moon has never landed on Mars. It is also true that electrons diffracting from crystals cannot be understood well using Newton's laws. So one must know when classical mechanics can be used and when quantum mechanics is necessary. The answer is provided by the uncertainty product $\Delta x \Delta p_x$.

Consider a piece of stone, a dust particle or a ball. When we talk of its position in normal laboratory conditions, what is the uncertainty in it? My measuring apparatus like meter scale, tape, vernier calliperse, etc., will never tell me position better than say a hundredth part of a millimeter. So take $\Delta x \approx 10^{-5}\,\mathrm{m}$. I am talking of values corresponding to very careful measurements, in many cases Δx will be much more than this. Similarly what accuracy do we expect in velocity measurement? Let me take it as say 10^{-6} m/s. If the mass of the particle is 1 mg, the uncertainty in momentum is $\Delta p_x = m\Delta v = 10^{-12}$ kg m/s. The uncertainty product in the above conditions is $\Delta x\, \Delta p_x = 10^{-17}\,\mathrm{J\,s}$. In the situations we generally encounter and even for many of the scientific experiments, the uncertainty product is much larger than this. Quantum mechanics sets a lower limit of $\hbar/2 \approx 10^{-34}\,\mathrm{J\,s}$. It warns you against trying to go below this limit. But who cares for such a limit? If the product is anyway going to be more than $10^{-17}\,\mathrm{J\,s}$, how does it matter whether there is a law forbidding us to go below $10^{-34}\,\mathrm{J\,s}$? Classical mechanics, which does not recognize any such limit, therefore gives very accurate results in such cases.

When we talk of an electron in an atom, the situation is different. The position uncertainty is of the order of the diameter of the atom ($\approx 10^{-10}\,\mathrm{m}$) and that in momentum is likewise small ($\approx 10^{-24}\,\mathrm{kg\,m/s}$) and the product is indeed close to the limit. The quantum mechanics is very active here and it forces you not to use classical mechanics in such cases.

5.7 You learned in this chapter

- For Dirac delta function type wave function of a particle, the position of the particle is precisely known but all momenta from $-\infty$ to $+\infty$ are equally probable.
- For plane wave type wave function, the momentum is precisely known but all values of the position from $-\infty$ to $+\infty$ are equally probable.
- Uncertainty in position is defined as

$$\Delta x = \left[\left\langle x^2\right\rangle - \langle x\rangle^2\right]^{1/2} \text{ where } \langle x\rangle = \int_{-\infty}^{\infty} x\,|\psi(x)|^2\,dx \text{ and } \left\langle x^2\right\rangle = \int_{-\infty}^{\infty} x^2\,|\psi(x)|^2\,dx.$$

- Uncertainty in momentum is defined as $\Delta p_x = \left[\left\langle p_x^2\right\rangle - \langle p_x\rangle^2\right]^{1/2}$

  where $\langle p_x\rangle = \int_{-\infty}^{\infty} p\,|a(p)|^2\,dp$, $\left\langle p_x^2\right\rangle = \int_{-\infty}^{\infty} p^2\,|a(p)|^2\,dp$

  and $a(p) = \dfrac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x)\,e^{-\frac{i}{\hbar}px}\,dx$.

- For any state of a particle $\Delta x\,\Delta p_x \geq \hbar/2$. This is called Heisenberg uncertainty principle.
- The uncertainty product is minimum, i.e., $\hbar/2$ for a Gaussian wave packet.
- In the situations where the uncertainty product is much larger than $\hbar$, laws of classical mechanics can be applied to get very good results.

Solved Problems

1. Using Heisenberg uncertainty principle, estimate the minimum possible energy of a linear harmonic oscillator of mass *m*. The potential for such a particle is $V(x) = m\omega^2x^2/2$.

Solution: In order to have an uncertainty of Δp_x, the value of the momentum itself should have at least a value comparable to Δp_x. You cannot have an uncertainty of 5 units if the value never exceeds 2 units. So we assume that $p \approx \Delta p_x$. Similarly $x \approx \Delta x$. The expression for energy is

$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$$

$$\approx \frac{(\Delta p_x)^2}{2m} + \frac{1}{2}m\omega^2(\Delta x)^2.$$

From uncertainty principle, $\Delta p_x \geq \dfrac{\hbar}{2\Delta x}$. As we are looking for the lowest energy, let us write

$\Delta p_x = \dfrac{\hbar}{2\Delta x}$,

$$E \approx \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}m\omega^2(\Delta x)^2.$$

For E to be minimum, $\dfrac{dE}{d(\Delta x)}$ should be zero. This gives,

$$(\Delta x)^2 = \frac{\hbar}{2m\omega} \text{ and } E_{\min} = \frac{\hbar\omega}{2}.$$

Incidentally, a rigorous analysis also shows that $\hbar\omega/2$ is the minimum possible energy of a linear harmonic oscillator. I do not claim that the method used above is accurate to give the exact value of the minimum energy. I knew the exact result and chose my approximations in such a way that the final result matched with the actual value.

2. The speedometer of a 180 kg vehicle reads 72 km/h at a particular instant. The readings are known to have an accuracy of ±2 km/h. What would be the minimum uncertainty in the position of the vehicle at that instant according to the Heisenberg Uncertainty Principle?

Solution: The uncertainty in the momentum is

$$\Delta p_x = \Delta(mv_x) = m\Delta v_x$$

$$= (180\,\text{kg}) \times (2\,\text{km/h})$$

$$= 100\,\text{kg.m/s}.$$

According to Heisenberg Uncertainty Principle, the uncertainty in the position Δx should satisfy

$$(\Delta x)(\Delta p_x) \geq \frac{\hbar}{2}.$$

Thus the minimum uncertainty in position is

$$(\Delta x)_{min} = \frac{\hbar}{2\Delta p_x} = \frac{10^{-34}\,\text{J.s}}{200\,\text{kg.m/s}} = 0.5 \times 10^{-36}\,\text{m}.$$

Remember the size of an atom is of the order of 10^{-10}m and that of a nucleus is 10^{-15}m. A size of 10^{-36}m is too small to detect with our present day technology and hence we can safely ignore it. Another comment is that I have not used the standard definition of Δp_x and so the value of $(\Delta x)_{min}$ obtained is not exact. However, the minimum would be only somewhat different from this and ignoring this is completely justified.

3. The speed of an electron $(m = 1.67 \times 10^{-31}\,\text{kg})$ is measured in an experiment to be 5×10^{6} m/s. The value from this measurement has an uncertainty of 10%. Estimate the minimum uncertainty in the position.

Solution: The uncertainty in speed is $\Delta v_x = 5 \times 10^{5}$ m/s. The uncertainty in momentum is therefore

$$\Delta p_x = m\Delta v_x = 1.67 \times 10^{-31} \times 5 \times 10^{5}\,\text{kg. m/s}$$

$$= 8.35 \times 10^{-26}\,\text{kg. m/s}.$$

The minimum uncertainty in position is about

$$(\Delta x)_{min} = \frac{\hbar}{2(\Delta p_x)} = \frac{10^{-34}}{2 \times 8.35 \times 10^{-26}} \approx 10^{-9}\,\text{m}.$$

So the uncertainty in position is about 1 nm which is quite signifanct with the modern technology.

4. Show that (a) $\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^*(x)\left[-i\hbar\frac{d}{dx}\right]\psi(x)\,dx$ (b) $\langle p_x^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x)\left[-\hbar^2\frac{d^2}{dx^2}\right]\psi(x)\,dx$.

Solution: (a) Expand $\psi(x)$ in terms of the momentum eigenfunctions,

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} a(p)e^{\frac{i}{\hbar}px}\,dp.$$

This gives,

$$\frac{d\psi}{dx} = \frac{1}{\sqrt{2\pi\hbar}}\frac{i}{\hbar}\int_{-\infty}^{\infty} p\,a(p)e^{\frac{i}{\hbar}px}\,dp. \qquad \text{(i)}$$

The right hand side of the equation given in the question is

$$I = \int_{-\infty}^{\infty} \psi^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi(x)\,dx$$

$$= \int_{-\infty}^{\infty}\left[\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} a^*(p_1)e^{-\frac{i}{\hbar}p_1 x}dp_1\right](-i\hbar)\frac{1}{\sqrt{2\pi\hbar}}\frac{i}{\hbar}\left[\int_{-\infty}^{\infty} p_2\, a(p_2)e^{\frac{i}{\hbar}p_2 x}dp_2\right]$$

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} a^*(p_1)\;\; p_2\, a(p_2)\left(\int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(p_2-p_1)x}dx\right)dp_1dp_2 . \qquad \text{(ii)}$$

Separate variables p_1 and p_2 are used in the two integrations on momentum. This can be done as we are doing definite integration and the integration variable is dummy. Out of the three integrations in (ii), I have decided to perform the x-integration first. So, the x-dependent terms are collected in the bracket. This integration is equal to $2\pi\hbar\,\delta(p_2-p_1)$ (Chapter 3). Thus,

$$I = \int_{-\infty}^{\infty} a^*(p_1)\left(\int_{-\infty}^{\infty} p_2\, a(p_2)\,\delta(p_2-p_1)\,dp_2\right)dp_1 .$$

This time I decided to perform integration on p_2 first and so all p_2-dependent terms are collected in the bracket. This gives,

$$I = \int_{-\infty}^{\infty} a^*(p_1)\, p_1\, a(p_1)dp_1$$

$$= \int_{-\infty}^{\infty} p_1\, |a(p_1)|^2\, dp_1 = \langle p_x\rangle .$$

(b) From (i),

$$\frac{d^2\psi}{dx^2} = \frac{1}{\sqrt{2\pi\hbar}}\left(-\frac{1}{\hbar^2}\right)\int_{-\infty}^{\infty} p^2\, a(p)e^{\frac{i}{\hbar}px}dp .$$

So the RHS of the equation given in the question is

$$I = \int_{-\infty}^{\infty}\left[\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} a^*(p_1)e^{-\frac{i}{\hbar}p_1 x}dp_1\right](-\hbar^2)\left[\frac{1}{\sqrt{2\pi\hbar}}\left(-\frac{1}{\hbar^2}\right)\int_{-\infty}^{\infty} p_2^2\, a(p_2)e^{\frac{i}{\hbar}p_2 x}dp_2\right]dx$$

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} a^*(p_1)\;\; p_2^2\, a(p_2)\left(\int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(p_2-p_1)x}dx\right)dp_1dp_2$$

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} a^*(p_1)\;\; p_2^2\, a(p_2)\;\; 2\pi\hbar\,\delta(p_2-p_1)dp_1dp_2$$

$$= \int_{-\infty}^{\infty} a^*(p_1)\left(\int_{-\infty}^{\infty} p_2^2\, a(p_2)\;\delta(p_2-p_1)dp_2\right)dp_1$$

$$= \int_{-\infty}^{\infty} a^*(p_1)\, p_1^2\, a(p_1)dp_1 = \int_{-\infty}^{\infty} p_1^2\, |a(p_1)|^2\, dp_1 \;\; = \langle p_x^2\rangle$$

5. The wave function of a particle at a given instant is

$$\psi(x) = \frac{1}{\sqrt{a}}e^{\frac{x}{a}+\frac{i}{\hbar}p_0 x} \qquad \text{for } x \le 0$$

$$= \frac{1}{\sqrt{a}}e^{-\frac{x}{a}+\frac{i}{\hbar}p_0 x} \qquad \text{for } x > 0$$

Find Δx and Δp_x.

Solution: You have already worked with this function in Chapter-4 (Exercises). The probability density $|\psi(x)|^2$ is symmetrical about $x = 0$ so the expectation value of x is $\langle x\rangle = 0$.

$$\langle x^2\rangle = \int_{-\infty}^{\infty} x^2 |\psi(x)|^2\, dx$$

$$= \int_{-\infty}^{0} x^2 \frac{1}{a} e^{2x/a}\, dx + \int_{0}^{\infty} x^2 \frac{1}{a} e^{-2x/a}\, dx$$

$$= \frac{2}{a}\int_{0}^{\infty} x^2 e^{-2x/a}\, dx = \frac{a^2}{2}.$$

Thus, $\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2} = a/\sqrt{2}$.

The momentum wave function $a(p)$ is given by (Chapter-4, Exercises)

$$a(p) = \sqrt{\frac{2\hbar^2}{\pi a^3}}\frac{1}{(p-p_0)^2 + (\hbar/a)^2}.$$

This function is symmetric about $p = p_0$, and so is $|a(p)|^2$. Thus $\langle p_x\rangle = p_0$. How do I get $\langle p_x^2\rangle$? I can get it by

$$\langle p_x^2\rangle = \int_{-\infty}^{\infty} p^2 |a(p)|^2\, dp.$$

But that will need a difficult integration. An easy way is to use the result of the previous problem.

$$\langle p_x^2\rangle = \int_{-\infty}^{\infty} \psi^*(x)\left(-\hbar^2 \frac{d^2}{dx^2}\right)\psi(x)dx.$$

As $\psi(x)$ is not differentiable at $x = 0$, I divide the integration in three parts.

$$\langle p_x^2\rangle = -\hbar^2\left[\int_{-\infty}^{-\epsilon} \psi^*(x)\frac{d^2}{dx^2}\psi(x)dx + \int_{-\epsilon}^{\epsilon} \psi^*(x)\frac{d^2}{dx^2}\psi(x)dx + \int_{\epsilon}^{\infty} \psi^*(x)\frac{d^2}{dx^2}\psi(x)dx\right]$$

$$= -\hbar^2\left[\int_{-\infty}^{-\epsilon} \frac{1}{\sqrt{a}} e^{\frac{x}{a} - \frac{i}{\hbar}p_0 x} \frac{1}{\sqrt{a}}\left(\frac{1}{a} + \frac{ip_0}{\hbar}\right)^2 e^{\frac{x}{a} + \frac{i}{\hbar}p_0 x} dx + \int_{-\epsilon}^{\epsilon} \psi^*(0)\frac{d^2\psi(x)}{dx^2}\, dx\right.$$
$$\left. + \int_{\epsilon}^{\infty} \frac{1}{\sqrt{a}} e^{-\frac{x}{a} - \frac{i}{\hbar}p_0 x} \frac{1}{\sqrt{a}}\left(-\frac{1}{a} + \frac{ip_0}{\hbar}\right)^2 e^{-\frac{x}{a} + \frac{i}{\hbar}p_0 x} dx\right]$$

$$= -\hbar^2\left[\frac{1}{a}\left(\frac{1}{a} + \frac{ip_0}{\hbar}\right)^2 \int_{-\infty}^{-\epsilon} e^{2x/a}dx + \psi^*(0)\left|\frac{d\psi}{dx}\right|_{-\epsilon}^{\epsilon} + \frac{1}{a}\left(-\frac{1}{a} + \frac{ip_0}{\hbar}\right)^2 \int_{\epsilon}^{\infty} e^{-2x/a}dx\right].$$

Now let $\epsilon \to 0$.

For $x < 0$,
$$\frac{d\psi}{dx} = \frac{1}{\sqrt{a}}\left(\frac{1}{a} + \frac{ip_0}{\hbar}\right)e^{\frac{x}{a} + \frac{i}{\hbar}p_0 x}$$

and for $x > 0$,
$$\frac{d\psi}{dx} = \frac{1}{\sqrt{a}}\left(-\frac{1}{a} + \frac{ip_0}{\hbar}\right)e^{-\frac{x}{a} + \frac{i}{\hbar}p_0 x}.$$

Thus as $\epsilon \to 0$,
$$\left.\frac{d\psi}{dx}\right|_{-\epsilon}^{\epsilon} = -\frac{2}{\sqrt{a}}\left(\frac{1}{a}\right).$$

So,
$$\langle p_x^2\rangle = -\hbar^2\left[\frac{1}{a}\left(\frac{1}{a}+\frac{ip_0}{\hbar}\right)^2\frac{a}{2}+\frac{1}{\sqrt{a}}\left(-\frac{2}{a\sqrt{a}}\right)+\frac{1}{a}\left(-\frac{1}{a}+\frac{ip_0}{\hbar}\right)^2\right]=p_0^2+\frac{\hbar^2}{a^2}.$$

Thus,
$$\Delta p_x = \sqrt{\langle p_x^2\rangle - \langle p_x\rangle^2} = \hbar/a .$$

EXERCISES

1. Using uncertainty principle, estimate the minimum possible energy of a particle moving in the potential $V(x) = V_0|x|/a$. **Ans.** $\frac{3}{2}\left(\frac{\hbar^2 V_0^2}{ma^2}\right)^{1/3}$

2. A nucleus has diameter of the order of few femtometers. Assuming that an electron resides inside the nucleus, estimate its minimum kinetic energy. Beta particles coming from radioactive nuclei have kinetic energy of the order of an MeV. Compare this with your result and convince yourself that electrons do not reside inside a nucleus. **Ans.** $\sim 10^5$ MeV

3. A particle of mass m is confined to a region $0 < x < L$. The potential energy of the particle is zero while it is in this region. Estimate the minimum possible energy. **Ans.** $\hbar^2/(2mL^2)$

4. The energy of a hydrogen atom is written in elementary analysis as
$$E = \frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r}$$
where p is the magnitude of the linear momentum and r is the distance of the electron from the proton (you need not assume a circular orbit, the electron can change its distance from the proton giving rise to uncertainly in radius). Assume the uncertainty Δr to be equal to the average value of r and the uncertainty Δp to be equal to the average value of p. Also assume $(\Delta r)(\Delta p)$ to have a value of $\hbar/2$ and find the average value of r in the ground state of hydrogen atom. **Ans.** $\frac{4\pi\epsilon_0\hbar^2}{me^2} = 53\,\text{pm}$

5. Using the assumptions given in the above problem, find the minimum value of the energy of a hydrogen atom in the ground state. **Ans.** $-\frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2} = -13.6\,\text{eV}$

6. Consider two wave functions: $\psi_1(x) = Ae^{-x^2/a^2}e^{ikx}$ and $\psi_2(x) = Be^{(x-b)^2/a^2}e^{2ikx}$. In which of the two, the uncertainty product $\Delta x\,\Delta p$ is larger, or is it the same in both the wave functions?

   Ans. Same, $\hbar/2$, as both of them are Gaussian wave packets

7. Show that the expectation value of x may be written as $\langle x\rangle = \int_{-\infty}^{\infty} a^*(p)\left(i\hbar\frac{d}{dp}\right)a(p)\,dp$ where $a(p)$ is the momentum wave function.

8. Show that the expectation value of x^2 may be written as $\langle x^2\rangle = \int_{-\infty}^{\infty} a^*(p)\left(-\hbar^2\frac{d^2}{dp^2}\right)a(p)\,dp$ where $a(p)$ is the momentum wave function.

9. The momentum wave function of a particle is given as $a(p) = \frac{1}{\sqrt{p_0}}\exp\left(-|p|/p_0\right)$. Find $\langle x\rangle$, $\langle x^2\rangle$, $\langle p_x\rangle$ and $\langle p_x^2\rangle$. Evaluate the uncertainty product $\Delta x\,\Delta p_x$. **Ans.** $0,\ \hbar^2/p_0^2,\ 0,\ p_0^2/2,\ \hbar/\sqrt{2}$

10. The momentum wave function of a particle is given by

$$a(p) = \frac{1}{\sqrt{p_0}}\,e^{\frac{p}{p_0}-\frac{i}{\hbar}x_0p} \quad \text{for } p \le 0$$

$$= \sqrt{\frac{1}{p_0}}\,e^{\frac{-p}{p_0}-\frac{i}{\hbar}x_0p} \quad \text{for } p > 0.$$

Find the uncertainty product $\Delta x\,\Delta p_x$. **Ans.** $\sqrt{2}\hbar$

11. The wave function of a particle at a given instant is given as

$$\psi(x) = \sqrt{\frac{3}{2a^3}}(a+x) \quad \text{for } -a < x < 0$$

$$= \sqrt{\frac{3}{2a^3}}(a-x) \quad \text{for } 0 < x < a$$

$$= 0 \qquad \text{otherwise}$$

Find the uncertainty product $\Delta x\,\Delta p_x$. **Ans.** $\sqrt{3/10}\hbar$

12. Consider wave function $\psi(x) = c\left(1-x^2\right)$ in some units for $-1 \le x \le 1$ and zero everywhere else. (a) Find the constant c so that the wave function is normalized. (b) Find Δx, Δp and the product $\Delta x\,\Delta p$.

Ans. (a) $\sqrt{15}/4$ **(b)** $\sqrt{\frac{1}{7}},\ \sqrt{\frac{5}{2}}\hbar,\ \sqrt{\frac{5}{14}}\hbar$

13. The momentum wave function of a particle is $a(p) = 1\sqrt{a}$, for $-a/2 \le p \le a/2$ and $= 0$ otherwise. What is the order of uncertainty in momentum? Show that as a is changed, the uncertainties in momentum and in position vary inversely to each other.

6

Multiplication is Position and Differentiation is Momentum—Operator Formulation I

6.1 The operator $-i\hbar\frac{d}{dx}$ for momentum

You have seen in the previous chapter (solved problems) that the expectation value of the linear momentum p_x can be written as

$$\langle p_x\rangle = \int_{-\infty}^{\infty}\psi^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi(x)\,dx$$

or

$$\langle p_x\rangle = \int_{-\infty}^{\infty}\psi^*(x)\,\mathrm{P_x}\,\psi(x)\,dx \tag{6.1}$$

where $\mathrm{P_x}$ is written for the operator $-i\hbar\frac{d}{dx}$. It operates on the function $\psi(x)$ to give another function $-i\hbar\frac{d\psi(x)}{dx}$. Thus

$$\mathrm{P_x} = -i\hbar\frac{d}{dx}$$

$$\mathrm{P_x}\psi(x) = -i\hbar\frac{d\psi(x)}{dx}.$$

Compare Equation 6.1 with those for expectation values of x, x^2, $f(x)$, etc.

$$\langle x\rangle = \int_{-\infty}^{\infty}\psi^*(x)\,x\,\psi(x)\,dx \tag{i}$$

$$\langle x^2\rangle = \int_{-\infty}^{\infty}\psi^*(x)\,x^2\,\psi(x)\,dx \tag{ii}$$

$$\langle f(x)\rangle = \int_{-\infty}^{\infty}\psi^*(x)\,f(x)\,\psi(x)\,dx \tag{iii}$$

Don't you feel that $\mathrm{P_x}$ of Equation 6.1 has a direct relation with the linear momentum p_x? All the equations above have similar mathematical structure. In the integrant, we have $\psi^*(x)$ and $\psi(x)$, and in between these we put x to get $\langle x\rangle$, x^2 to get $\langle x^2\rangle$, $f(x)$ to get $\langle f(x)\rangle$ and $\mathrm{P_x}$ to get $\langle p_x\rangle$. It strongly provokes us to identify $\mathrm{P_x}$ with the linear momentum p_x.

But $\mathrm{P_x}$ is written for $-i\hbar\frac{d}{dx}$. It is a mathematical operator, essentially differentiation with respect to x. Its job is to operate on a function $f(x)$ and give us a new function. For example, if $f(x) = e^{-x^2/a^2}$,

$$P_x f(x) = P_x\left(e^{-x^2/a^2}\right) = -i\hbar\frac{d}{dx}\left(e^{-x^2/a^2}\right) = \frac{2i\hbar}{a^2}x\,e^{-x^2/a^2}.$$

Figure 6.1 shows the shapes of $f(x)$ and $-iP_x f(x)$ in this case. Note that I cannot plot $P_x f(x)$ as it is complex.

So P_x itself is not the linear momentum but it is closely related to that. We call it *linear momentum operator* or simply *momentum operator*. The suffix x reminds us that we are talking of the x-component of momentum.

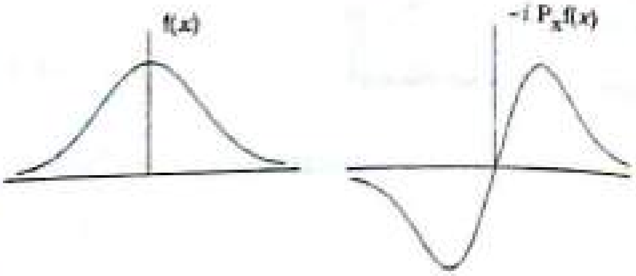


Fig. 6.1

In general, the function $P_x\psi(x)$, where $\psi(x)$ is the wave function of the particle, does not seem to have a special interpretation. But if the wave function of the particle at the given instant happens to be an eigenfunction of the linear momentum, $P_x\psi(x)$ does have a special interpretation. The wave function of a particle for which the linear momentum is known to be p_0 (hypothetical situation), is given by

$$\phi(x) = Ae^{\frac{i}{\hbar}p_0x}.$$

This is a pure state for the momentum measurement. If the particle has this wave function and an ideal momentum measurement is made, we are sure to get the value p_0. Also the measurement will not change the wave function which will remain $\phi(x)$. Let us see what happens if P_x operates on $\phi(x)$.

$$P_x\phi(x) = -i\hbar\frac{d}{dx}(Ae^{\frac{i}{\hbar}p_0x}) = p_0\,Ae^{\frac{i}{\hbar}p_0x}$$

or

$$P_x\phi(x) = p_0\,\phi(x). \tag{6.2}$$

We see that when P_x operates on $\phi(x)$, the functional form remains the same, the function is only multiplied by a constant p_0. In general, P_x changes the shape of the function. Look at Figure 6.1 once again to check this. But, for the function used in Equation 6.2, operation of P_x does not change the functional form, it simply multiplies it by a constant. And what is that constant? It is the value of linear momentum in that state.

Show Equation 6.2 to a mathematician and he/she will tell you, "It is an eigenvalue equation". If an operator A operates on a function $f(x)$ and gives back the same function multiplied by a constant, that is, if

$$A\,f(x) = a\,f(x)$$

then $f(x)$ is called an *eigenfunction* of A and a is called the *eigenvalue* of A corresponding to this eigenfunction $f(x)$.

The function $Ae^{\frac{i}{\hbar}p_0x}$ is an eigenfunction of P_x and p_0 is the corresponding eigenvalue. Denoting the state represented by wave function by $|p_0\rangle$, Equation 6.2 can be written as

$$P_x|p_0\rangle = p_0|p_0\rangle. \tag{6.3}$$

The state represented by an eigenfunction of an operator is also called an *eigenstate* of that operator.

6.2 The operator for position

The expectation value of position of a particle in a state given by the wave function $\psi(x)$ is

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

We can write it as

$$\langle x\rangle = \int_{-\infty}^{\infty} \psi^*(x)\, \mathrm{X}\, \psi(x)\, dx \tag{6.4}$$

where X is written for multiplication by x. Equation 6.4 resembles Equation 6.1 if you treat X as an operator, the operation being multiplication by x. Then

$$\mathrm{X}\, f(x) = x\, f(x).$$

X operating on $f(x)$ gives a new function $x\, f(x)$. For example, $\mathrm{X}e^{-x} = xe^{-x}$. The function xe^{-x} is quite different from the function e^{-x}. Operation by an operator in general changes the functional form.

The operator X corresponds to the position in the same way as P_x corresponds to linear momentum. We call it *position operator.*

If the position of a particle is precisely known to be, say, x_0 (hypothetical case), its wave function is given by

$$\phi(x) = c\, \delta(x - x_0). \tag{i}$$

The definite momentum wave function was shown to be an eigenfunction of momentum operator P_x. Is the definite position wave function given by (i) an eigenfunction of the position operator X? Yes, it is. Let me show this.

$$\mathrm{X}\, \phi(x) = x\, \phi(x) = x\, c\, \delta(x - x_0). \tag{ii}$$

In chapter 3, I solved a problem showing that

$$x\, \delta(x - x_0) = x_0\, \delta(x - x_0).$$

Using this, Equation (ii) becomes

$$\mathrm{X}\, \phi(x) = x_0\, \phi(x) \tag{6.5}$$

or

$$\mathrm{X}|x_0\rangle = x_0|x_0\rangle. \tag{6.6}$$

A definite position wave function is indeed an eigenfunction of the position operator and the value of position (x_0 here) is the corresponding eigenvalue.

How many eigenfunctions are there for X? Infinity. These are of the form $c\,\delta(x - x_0)$ and x_0 can take any value from $-\infty$ to $+\infty$. For any given x_0, c can also be taken differently but that does not change the form or shape of the function and is not considered as a separate eigenfunction.

You know that a wave function can be written as a linear combination of delta functions with different values of x_0. That means: *Any wave function of a particle can be written as a linear combination of the eigenfunctions of the position operator.*

And how many eigenfunctions are there for P_x? Again infinity. These are plane waves like $Ae^{\frac{i}{\hbar}p_0 x}$ and p_0 can take any value. You also know that any wave function $\psi(x)$ can be written as a linear combination of plane waves with different values of p_0. That means: *Any wave function of a particle can be written as a linear combination of the eigenfunctions of the momentum operator.*

Do we have operators for variables other than position and momentum? Yes. For each measurable quantity, we have an operator.

6.3 Operator Formulation

The operator X (multiplication by x) is associated with the measurable physical quantity 'position', and P_x (that is, $-i\hbar\frac{d}{dx}$) is associated with the measurable physical quantity 'momentum'. In each case the eigenvalues of the operator represent the possible results of measurement of the corresponding physical quantity and the eigenfunctions of the operator represent the states in which that quantity has a definite value. In fact, each measurable physical quantity, called a dynamical variable, has a corresponding operator with such properties. Let me give a more formal description of the relation between the physically measurable quantities and operators.

(a) For any physically measurable quantity a, which we call a dynamical variable, there is associated an operator A.

(b) Eigenvalues of A are the only possible results of measurement of the quantity a.

(c) The eigenfunctions of A represent the states of the particle in which the value of the quantity a is precisely known. We say that a has a definite value in such a state.

(d) If the wave function of the system before the measurement of a happens to be an eigenfunction of A, the result of the measurement is sure to be the corresponding eigenvalue.

(e) If the wave function of the particle before the measurement is not an eigenfunction of A, the result of measurement cannot be predicted beforehand with certainty.

(f) If the measurement gives a result a_0, the wave function just after the measurement becomes an eigenfunction of A corresponding to the eigenvalue a_0, irrespective of what it was before the measurement. This principle is called *'collapse of wave function in a measurement'*.

(g) Any wave function $\psi(x)$ can be written as a linear combination of the eigenfunctions of A. If the eigenvalues a_i of A are discrete, and $\phi_i(x)$ represent the eigenfunctions of A, the wave function $\psi(x)$ can be written as $\psi(x) = \sum_i c_i\phi_i(x)$ where c_i's are constants (independent of x).

(h) If the eigenvalues a of A are continuous (from $-\infty$ to $+\infty$), and $\phi(x,a)$ represent the eigenfunctions of A, the wave function $\psi(x)$ can be written as $\psi(x) = \int_{-\infty}^{\infty} c(a)\,\phi(x,a)\,da$.

(i) The probability of getting a particular value in the measurement of a is related to the coefficients of expansion c_i or $c(a)$.

Most of the ideas discussed in these statements were introduced time to time in previous chapters. Here the things are written in more formal way and in terms of operators. I would advice you to read Sections 4.1 and 4.2 once again and compare with the above description.

6.4 Operators for some of the measurable quantities

The procedure for writing the expression for the operator of a dynamic variable is simple. Write the expression of the variable in terms of position x and momentum p_x. Then replace x by the operator X, and p_x by the operator $P_x = i\hbar\frac{d}{dx}$ in this expression. In general, you will get the expression for the operator. But there are some cases in which this procedure does not give the correct expression for the operators concerned. I will talk about such cases later.

I am giving below some of the commonly used measurable quantities and the corresponding operators. And remember, I am talking in one dimension. For the present, the space means only the x-axis. The operators given here correspond to the variables we commonly encounter while discussing 1-D motion of a particle.

Quantity	**Operator**	**Symbol**
Position	Multiplication by x	X
Linear momentum (x-component)	$-i\hbar\dfrac{d}{dx}$	P_x
Kinetic energy	$-\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$	K
Potential energy	Multiplication by $V(x)$	V
Total mechanical energy	$-\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}+V(x)$	H

6.5 You learned in this chapter

- With each physically measurable quantity there is associated an operator.
- The operator for position is multiplication by x and that for linear momentum is $P_x = -i\hbar\dfrac{d}{dx}$.
- The eigenvalues and eigenfunctions of the operator corresponding to a variable have intimate relations with the measurement of that variable. These relations are given in section 6.3.

Solved Problems

1. Let the wave function of a particle of mass m at a given instant be $\psi(x) = Ae^{-x^2/a^2}$. What will be the function $K\psi(x)$ where K is the kinetic energy? Is this wave function an eigenfunction of kinetic energy?

Solution: The kinetic energy operator is $K = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$. Thus

$$K\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left(Ae^{-x^2/a^2}\right)$$

$$= -\frac{\hbar^2}{2m}\frac{d}{dx}\left[-\frac{2A}{a^2}xe^{-x^2/a^2}\right]$$

$$= \frac{2A\hbar^2}{2ma^2}\left[x\left(\frac{-2x}{a^2}e^{-x^2/a^2}\right)+e^{-x^2/a^2}\right]$$

$$= \frac{A\hbar^2}{ma^2}\left(1-\frac{2x^2}{a^2}\right)e^{-x^2/a^2}.$$

This is not an eigenfunction of kinetic energy.

2. A particle of mass m is subjected to the potential energy $V(x)=\frac{1}{2}kx^2$. At a particular time, it has the wave function $\psi(x)=Axe^{-x^2/a^2}$. If the particle has a definite total mechanical energy, find the value of a.

Solution: The operator corresponding to the total mechanical energy is $H=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)$. If the particle has definite value of the total mechanical energy, its wave function should be an eigenfunction of H. that is,

$$H\psi(x)=\lambda\psi(x) \text{ where } \lambda \text{ is independent of } x.$$

$$H\psi(x)=\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}kx^2\right]\left[Axe^{-x^2/a^2}\right]$$

$$=-\frac{A\hbar^2}{2m}\frac{d^2}{dx^2}\left(xe^{-x^2/a^2}\right)+\frac{1}{2}kAx^3e^{-x^2/a^2}$$

$$=-\frac{A\hbar^2}{2m}\frac{d}{dx}\left[\left(1-\frac{2x^2}{a^2}\right)e^{-x^2/a^2}\right]+\frac{1}{2}kAx^3e^{-x^2/a^2}$$

$$=-\frac{A\hbar^2}{2m}\left[\left(1-\frac{2x^2}{a^2}\right)\left(-\frac{2x}{a^2}\right)-\frac{4x}{a^2}\right]e^{-x^2/a^2}+\frac{1}{2}kAx^3e^{-x^2/a^2}$$

$$=-\frac{A\hbar^2}{2m}\left[-\frac{6x}{a^2}+\frac{4x^3}{a^4}\right]e^{-x^2/a^2}+\frac{1}{2}kAx^3e^{-x^2/a^2}$$

$$=\frac{3A\hbar^2}{ma^2}xe^{-x^2/a^2}-\left(\frac{2A\hbar^2}{ma^4}-\frac{1}{2}kA\right)x^3e^{-x^2/a^2}$$

If $H\psi(x)$ has to have the same functional form as $\psi(x)$, one should not have the $x^3e^{-x^2/a^2}$ term. So,

$$\frac{2A\hbar^2}{ma^4}-\frac{1}{2}kA=0$$

or, $$a=\left[-\frac{4\hbar^2}{mk}\right]^{1/4}.$$

EXERCISES

1. Let $\phi(x)=Ae^{-x^2/a^2}$. Show that the wave functions $X\phi(x)$ and $P_x\phi(x)$ represent the same state of a particle.
2. Find $\phi(x)$ for which $X\phi(x)=-(ia^2/\hbar)P_x\phi(x)$. Here a is a real positive quantity. **Ans.** $\phi_0e^{-x^2/(2a^2)}$
3. Let $\psi(x)=Ae^{\left(-\frac{x^2}{a^2}+ikx\right)}$. Find the values of $\psi(x)$, $X\psi(x)$ and $P_x\psi(x)$ at $x=0$. **Ans.** $A, 0, A\hbar k$
4. Let $\psi(x)=\frac{1}{\sqrt{a}}e^{-|x|/a}$. Sketch the function $P_x\psi(x)$.

5. Find the eigenfunctions of P_x by solving the differential equation $P_x\phi(x) = \lambda\phi(x)$.

6. Is the function $\psi(x) = Ae^{-x/a}$ an eigenfunction of the kinetic energy operator of a particle? **Ans.** No.

7. Show that $\psi(x) = Ae^{ikx}$ is an eigenfunction of the kinetic energy operator and find the corresponding eigenvalue. **Ans.** $\frac{\hbar^2k^2}{2m}$

8. Expand the function $\psi(x) = A\sin kx \sin 2kx$ as a linear combination of eigenfunctions of the momentum operator P_x. **Ans.** $\frac{A}{4}\left(-e^{-3ikx} + e^{-ikx} + e^{ikx} - e^{3ikx}\right)$

9. The eigenvalues of energy for a particle are E_0, E_1, ... and the corresponding eigenfunctions are $|\phi_0\rangle$, $|\phi_1\rangle$, ...
If a measurement of energy yields E_0 what would be the wave function just after the measurement? **Ans** $|\phi_0\rangle$

10. Find the eigenfunctions of the operator $X + \frac{i}{\hbar}P_x$. **Ans** $\psi_0 e^{-(x-\lambda)^2/2}$ where λ is a constant

7

Mathematics of Operators—Operator Formulation II

The physical quantities like position, linear momentum, kinetic energy, etc., have certain operators associated with them. Operators are mathematical actions on functions which produce new functions. Thus squaring can be an operator, differentiating can be another operator and so on. The operators corresponding to physically measurable quantities have some special properties. These operators belong to a class of operators called *Hermitian operators*. I will first define some general properties of operators and then tell you what a Hermitian operator is. The operators act on functions. For us, these functions are possible wave functions. While discussing operators you should keep in mind that they are supposed to act on those functions only which are possible wave functions of a particle, i.e., which are finite, continuous and square integrable. In other words the operators corresponding to the physical quantities are defined for functions in the state space F.

7.1 Linear operators

Suppose A is an operator. It is called a linear operator if it satisfies the following two conditions for arbitrary functions $f(x)$, $g(x)$ and arbitrary constant c.

(a) $A[f(x)+g(x)] = A[f(x)] + A[g(x)]$

(b) $A[cf(x)] = c[Af(x)]$.

According to the first condition, you add two functions $f(x)$, $g(x)$ and then operate A on the resulting function, or, you operate A on $f(x)$ and $g(x)$ separately and then add, you should end up with the same function. The second condition says that you multiply a function by a constant c and then operate A on the resulting function, or, you operate A on the function and then multiply by c, you should end up with the same function.

Example 7.1

Check whether the following operators are linear or not: (a) Multiplication by x, (b) Squaring.

Solution: (a) Let $f(x)$ and $g(x)$ be two functions of x. Let A denote the operator "multiplication by x"

$$A[f(x)+g(x)] = x[f(x)+g(x)] = xf(x) + xg(x) = A[f(x)] + A[g(x)]$$

$$A[cf(x)] = x[cf(x)] = cxf(x) = c[Af(x)].$$

Both the required conditions are satisfied. Hence, A is a linear operator.

(b) Let A denote the operator "squaring".

$$A[f(x)+g(x)] = [f(x)+g(x)]^2$$

$$A[f(x)] = [f(x)]^2, \quad A[g(x)] = [g(x)]^2.$$

We see that $A[f(x)+g(x)] \neq A[f(x)] + A[g(x)]$.

So, A is not a linear operator.

You can check that the second condition is also not fulfilled.

7.2 Operator algebra

When you did addition, subtraction, multiplication and division on numbers, your primary school teacher said she was teaching you *arithmetic*. Then your middle or high school teacher taught you the same operations on functions of x (perhaps expressions was the term used then) and called it *algebra*. At college level you were taught addition and multiplication of vectors and that went under the name *vector algebra* and today again I am telling you about addition and multiplication which form *operator algebra*.

If there are two operators A and B and an arbitrary constant c we define three new operators $\mathrm{A}+\mathrm{B}$, AB and cA as follows:

$$(\mathrm{A}+\mathrm{B})\,f(x)=\mathrm{A}\left[f(x)\right]+\mathrm{B}\left[f(x)\right] \tag{7.1}$$

$$(\mathrm{AB})\,f(x)=\mathrm{A}\left[\mathrm{B}f(x)\right] \tag{7.2}$$

and

$$(c\mathrm{A})\left[f(x)\right]=c\left[Af(x)\right]. \tag{7.3}$$

Here $f(x)$ is an arbitrary function. AA is written as A^2, AAA as A^3 and so on.

You can guess how I will define A − B. The operator −B is the same as (−1) B and A − B is the same as A + (−B).

Example 7.2

Let A = x *(that is, multiplication by x) and* B = $\dfrac{d}{dx}$. *Find* (A + B) sin x, (B + A) sin x, (AB) sin x *and* (BA) sin x.

Solution: $(\mathrm{A}+\mathrm{B})\sin x=\mathrm{A}(\sin x)+\mathrm{B}(\sin x) \;=\; x(\sin x)+\dfrac{d}{dx}(\sin x)=x\sin x+\cos x$

$$(\mathrm{B}+\mathrm{A})\sin x=\mathrm{B}(\sin x)+\mathrm{A}(\sin x)=\frac{d}{dx}(\sin x)+x(\sin x)=\cos x+x\sin x$$

$$(\mathrm{AB})\sin x=\mathrm{A}\left[\mathrm{B}(\sin x)\right]=x\left[\frac{d}{dx}(\sin x)\right]=x\cos x$$

$$(\mathrm{BA})\sin x=\mathrm{B}\left[\mathrm{A}(\sin x)\right]=\frac{d}{dx}\left[x(\sin x)\right]=x\cos x+\sin x.$$

From Example 7.2 you see that the product of operators, as defined above, is not commutative. The operators AB and BA are, in general, not the same. Addition of operators is commutative.

It is not that AB and BA are always different. You can verify that if $\mathrm{A}=\dfrac{d}{dx}$ and $\mathrm{B}=\dfrac{d^2}{dx^2}$, AB = BA. In general, if one of the two operators is multiplication-type and the other is differentiation-type, they do not commute $(\mathrm{AB}\neq\mathrm{BA})$. If both are multiplication-type or both are differentiation-type they commute (AB = BA).

If A and B are two operators we can construct an operator C = AB − BA. This operator is given a separate symbol [A, B] and is called the *commutator* of A with B. If the two operators A and B commute, [A, B] operating on any function is zero. Such an operator (always giving zero when operated) is called *zero operator*.

Example 7.3

Simplify $[X, P_x]$ *where* X *and* P_x *are operators corresponding to the position and the x-componen of linear momentum of a particle.*

Solution: $X = x$ and $P_x = -i\hbar \frac{d}{dx}$.

Let $f(x)$ be any function of x. then

$$[X, P_x]f(x) = [XP_x - P_xX]f(x)$$
$$= (XP_x)f(x) - (P_xX)f(x)$$
$$= \left(-i\hbar x\frac{d}{dx}\right)f(x) - \left(-i\hbar\frac{d}{dx}x\right)f(x)$$
$$= -i\hbar x\frac{df}{dx} + i\hbar\frac{d}{dx}(xf)$$
$$= -i\hbar x\frac{df}{dx} + i\hbar\left(x\frac{df}{dx} + f\right)$$
$$= i\hbar f(x).$$

Example 7.3 shows that $[X, P_x]$ operating on any function $f(x)$ just multiplies the function by $i\hbar$. We therefore write

$$[X, P_x] = i\hbar. \tag{7.4}$$

7.2.1 Two important commutation relations

$$[A, BC] = B[A, C] + [A, B]C \tag{7.5}$$

L.H.S. = $[A, BC] = A(BC) - (BC)A = ABC - BCA$.

R.H.S. = $B(AC - CA) + (AB - BA)C$

$= BAC - BCA + ABC - BAC = ABC - BCA$.

Thus L.H.S. = R.H.S. Note that in opening the brackets I have made sure that the order of the operators is not changed. Similarly, you can prove that

$$[AB, C] = A[B, C] + [A, C]B. \tag{7.6}$$

I will be using these two results extensively and so practice them well.

7.3 Hermitian operators

Consider an operator A which can act on the functions in the state space F. Consider any two functions $\psi_1(x)$ and $\psi_2(x)$ from this set. The operator A is called a Hermitian operator if

$$\langle (A\psi_1) | \psi_2 \rangle = \langle \psi_1 | (A\psi_2) \rangle. \tag{7.7}$$

Writing the scalar products in the integral form, this condition is

$$\int_{-\infty}^{\infty} [A\psi_1(x)]^* \psi_2(x)\,dx = \int_{-\infty}^{\infty} \psi_1^*(x)[A\psi_2(x)]\,dx. \tag{7.8}$$

This scalar product is written as $\langle\psi_1|A|\psi_2\rangle$. The operator A is written between two vertical lines. On one side of A you have the first function $\psi_1(x)$ and on the other side you have $\psi_2(x)$. If you think that the operator A is attached to $\psi_2(x)$, then $\langle\psi_1|A|\psi_2\rangle$ would be the scalar product of ψ_1 with $A\psi_2$. That is the RHS in Equation 7.7. You can also interpret that A is attached to $\psi_1(x)$. In that case the symbol $\langle\psi_1|A|\psi_2\rangle$ would be the scalar product of $A\psi_1(x)$ with $\psi_2(x)$. That is the LHS in Equation 7.7. If A is Hermitian, both are the same.

You can also think that the bra corresponding to $A|\psi_1\rangle$ is $\langle\psi_1|A$. Then the scalar product of $A|\psi_1\rangle$ with $|\psi_2\rangle$ is simply $\langle\psi_1|A|\psi_2\rangle$. You can verify that

$$\langle\psi_1|A|\psi_2\rangle = \langle\psi_2|A|\psi_1\rangle^* \tag{7.9}$$

for a Hermitian operator A. The RHS is

$$\left[\int_{-\infty}^{\infty}[A\psi_2(x)]^*\,\psi_1(x)\,dx\right]^* \qquad \text{[link A with } \psi_2(x) \text{ in the RHS of Equation 7.9]}$$

$$= \int_{-\infty}^{\infty}[A\psi_2(x)]\psi_1^*(x)\,dx$$

$$= \int\psi_1^*(x)[\,A\psi_2(x)]\,dx$$

$$= \text{LHS}. \qquad \text{[link A with } \psi_2(x) \text{ in the LHS of Equation 7.9]}$$

7.3.1 Hermitian adjoint

Take any two wave functions $\psi_1(x)$ and $\psi_2(x)$ and an operator A. In general,

$$\langle(A\psi_1)|\psi_2\rangle \neq \langle\psi_1|(A\psi_2)\rangle.$$

It is possible to find another operator B such that

$$\langle(B\psi_1)|\psi_2\rangle = \langle\psi_1|(A\psi_2)\rangle. \tag{7.10}$$

The operator B is called *Hermitian adjoint* of A.

If A is itself Hermitian,

$$\langle(A\psi_1)|\psi_2\rangle = \langle\psi_1|(A\psi_2)\rangle.$$

Comparing this with Equation 7.10 above, B = A. The Hermitian adjoint of A is the operator A itself. Thus a Hermitian operator is self-adjoint.

Even if an operator A is not Hermitian, I can use the symbol $\langle\psi_1|A|\psi_2\rangle$. If the interpretation is to attach A to $\psi_2(x)$ it is fine. The quantity is just $\langle\psi_1|(A\psi_2)\rangle$. So,

$$\langle\psi_1|A|\psi_2\rangle = \int_{-\infty}^{\infty}\psi_1^*(x)[A\psi_2(x)]\,dx.$$

But if you wish to attach A with $\psi_1(x)$, take the Hermitian adjoint of A and operate that on $\psi_1(x)$. You then get $\langle(B\psi_1)|\psi_2\rangle$. From Equation 7.10 these two are equal.

The Hermitian adjoint of A is written as $A^\dagger$. You read it as "A dagger". Thus, (7.11)

$$\langle A^\dagger\psi_1|\psi_2\rangle = \langle\psi_1|A\psi_2\rangle.$$

7.3.2 Some properties of Hermitian adjoints

(a) $(A^\dagger)^\dagger = A$

Let $|\psi_1\rangle$ and $|\psi_2\rangle$ be two arbitrary functions. By the definition of adjoint,

$$\left\langle A^\dagger\psi_1\middle|\psi_2\right\rangle = \langle\psi_1|A\psi_2\rangle.$$

Taking complex conjugates on both sides,

$$\left\langle \psi_2\middle|A^\dagger\psi_1\right\rangle = \langle A\psi_2|\psi_1\rangle. \tag{i}$$

By the definition of adjoint,

$$\left\langle \psi_2\middle|A^\dagger\psi_1\right\rangle = \left\langle (A^\dagger)^\dagger\psi_2\middle|\psi_1\right\rangle. \tag{ii}$$

Comparing (i) and (ii),

$$(A^\dagger)^\dagger = A. \tag{7.12}$$

(b) $(A+B)^\dagger = A^\dagger + B^\dagger$

Let $|\psi_1\rangle$ and $|\psi_2\rangle$ be two arbitrary functions. By the definition of adjoint,

$$\langle\psi_1|(A+B)\psi_2\rangle = \left\langle (A+B)^\dagger\psi_1\middle|\psi_2\right\rangle. \tag{iii}$$

Also,

$$\begin{aligned}\langle\psi_1|(A+B)\psi_2\rangle &= \langle\psi_1|A\psi_2 + B\psi_2\rangle\\ &= \langle\psi_1|A\psi_2\rangle + \langle\psi_1|B\psi_2\rangle\\ &= \left\langle A^\dagger\psi_1\middle|\psi_2\right\rangle + \left\langle B^\dagger\psi_1\middle|\psi_2\right\rangle\\ &= \left\langle A^\dagger\psi_1 + B^\dagger\psi_1\middle|\psi_2\right\rangle\\ &= \left\langle \left(A^\dagger + B^\dagger\right)\psi_1\middle|\psi_2\right\rangle. \end{aligned} \tag{iv}$$

Comparing (iii) and (iv),

$$(A+B)^\dagger = A^\dagger + B^\dagger. \tag{7.13}$$

(c) $(AB)^\dagger = B^\dagger A^\dagger$

Let $|\psi_1\rangle$ and $|\psi_2\rangle$ be two arbitrary functions. By the definition of adjoint,

$$\langle\psi_1|(AB)\psi_2\rangle = \left\langle (AB)^\dagger\psi_1\middle|\psi_2\right\rangle. \tag{v}$$

Also,

$$\begin{aligned}\langle\psi_1|(AB)\psi_2\rangle &= \langle\psi_1|A(B\psi_2)\rangle\\ &= \left\langle A^\dagger\psi_1\middle|B\psi_2\right\rangle\\ &= \left\langle B^\dagger(A^\dagger\psi_1)\middle|\psi_2\right\rangle\\ &= \left\langle \left(B^\dagger A^\dagger\right)\psi_1\middle|\psi_2\right\rangle. \end{aligned} \tag{vi}$$

Comparing (v) and (vi),

$$(AB)^\dagger = B^\dagger A^\dagger . \qquad (7.14)$$

7.4 You learned in this chapter

- An operator A is called a linear operator if for arbitrary $\psi_1(x)$, $\psi_2(x)$ and c,
  $A[\psi_1(x) + \psi_2(x)] = A[\psi_1(x)] + A[\psi_2(x)]$ and $A[c\psi_1(x)] = c[A\psi_1(x)]$.
- The operators (A+B), (AB) and (cA) are defined by
  $(A + B)\psi(x) = A[\psi(x)] + B[\psi(x)]$
  $(AB)\psi(x) = A[B\psi(x)]$
  $(cA)\psi(x) = c[A\psi(x)]$.
- The operator AB − BA is called the commutator of A with B and written as [A, B].
- $[X, P_x] = i\hbar$ where X = position operator and P_x = momentum operator (corresponding to x-direction).
- An operator A is called a Hermitian operator if for arbitrary $|\psi_1\rangle$ and $|\psi_2\rangle$ $\langle A\psi_1|\psi_2\rangle = \langle\psi_1|A\psi_2\rangle$. Each of these is written as $\langle\psi_1|A|\psi_2\rangle$.
- For a Hermitian operator A, $\langle\psi_1|A|\psi_2\rangle = \langle\psi_2|A|\psi_1\rangle^*$.
- If $\langle B\psi_1|\psi_2\rangle = \langle\psi_1|A\psi_2\rangle$ for arbitrary $|\psi_1\rangle$ and $|\psi_2\rangle$, then B is called the Hermitian adjoint of A. It is written as $A^\dagger$. Thus $\left\langle A^\dagger\psi_1\middle|\psi_2\right\rangle = \langle\psi_1|A\psi_2\rangle$. Each of these is written as $\langle\psi_1|A|\psi_2\rangle$.
- $(A^\dagger)^\dagger = A$, $(A+B)^\dagger = A^\dagger + B^\dagger$, $(AB)^\dagger = B^\dagger A^\dagger$.

Solved Problems

1. An operator A is defined as $A\,\psi(x) = \psi^*(x)\,\psi(x)$. Is this a linear operator?

Solution: For the given operator,

$$\begin{aligned} A[\psi_1(x)+\psi_2(x)] &= [\psi_1(x)+\psi_2(x)]^*\,[\psi_1(x)+\psi_2(x)] \\ &= [\psi_1^*(x)+\psi_2^*(x)]\,[\psi_1(x)+\psi_2(x)] \\ &= \psi_1^*(x)\,\psi_1(x)+\psi_2^*(x)\,\psi_2(x)+\psi_1^*(x)\,\psi_2(x)+\psi_2^*(x)\,\psi_1(x) \end{aligned}$$

and $\quad A\psi_1(x) + A\psi_2(x) = \psi_1^*(x)\psi_1(x) + \psi_2^*(x)\psi_2(x)$.

Thus, $\quad A[\psi_1(x)+\psi_2(x)] \neq A\psi_1(x) + A\psi_2(x)$ and hence A is not a linear operator.

2. Let $\psi(x) = Ae^{-x^2/a^2}$. Find $\langle\psi|P_x|\psi\rangle$.

Solution: $\quad \psi(x) = Ae^{-x^2/a^2}$.

So, $\quad P_x\psi(x) = -i\hbar\dfrac{d}{dx}\left(Ae^{-x^2/a^2}\right) = \dfrac{2i\hbar}{a^2}\,x\,A\,e^{-x^2/a^2}$.

$$\langle\psi|P_x|\psi\rangle = \int_{-\infty}^{\infty}\psi^*(x)[P_x\psi(x)]\,dx$$

$$= \int_{-\infty}^{\infty}\left(Ae^{-x^2/a^2}\right)\left[\frac{2i\hbar}{a^2}xe^{-x^2/a^2}\right]dx$$

$$= \frac{2i\hbar A}{a^2}\int_{-\infty}^{\infty} x\,e^{-2x^2/a^2}\,dx$$

$$= 0.$$

It is so, because the integrant is an odd function. Its value at x is the negative of that at $-x$. The integration is to be carried out from $-\infty$ to ∞, so, the positive and negative contributions cancel out. This is shown graphically in Figure 7.W1. Here y represents the integrand.

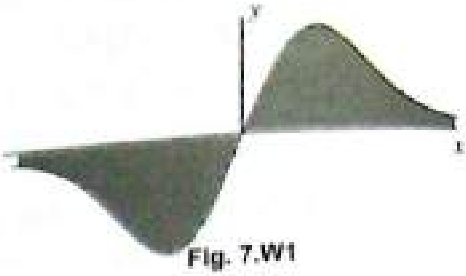


Fig. 7.W1

3. Show that $-i\hbar\frac{d}{dx}$ is a Hermitian operator but $\frac{d}{dx}$ is not.

Solution: The given operator $-i\hbar\frac{d}{dx}$ is the same as P_x. Let $\psi_1(x)$ and $\psi_2(x)$ be two arbitrary functions.

$$\langle\psi_1|P_x\psi_2\rangle = \int_{-\infty}^{\infty}\psi_1^*(x)\left[-i\hbar\frac{d}{dx}\psi_2(x)\right]dx$$

$$= -i\hbar\int_{-\infty}^{\infty}\psi_1^*(x)\frac{d}{dx}\psi_2(x)\,dx.$$

Integrating by parts, this is equal to

$$-i\hbar\left[\psi_1^*(x)\psi_2(x)\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\frac{d\psi_1^*(x)}{dx}\psi_2(x)\,dx\right].$$

For the wave function to be square integrable, it must go to zero as x goes to $-\infty$ or $+\infty$. Thus, the first term in the square bracket is zero. So,

$$\langle\psi_1|P_x\psi_2\rangle = i\hbar\int_{-\infty}^{\infty}\frac{d\psi_1^*(x)}{dx}\psi_2(x)\,dx. \tag{i}$$

Also,

$$\langle P_x\psi_1|\psi_2\rangle = \int_{-\infty}^{\infty}[P_x\psi_1(x)]^*\,\psi_2(x)\,dx$$

$$= \int_{-\infty}^{\infty}\left[-i\hbar\frac{d\psi_1(x)}{dx}\right]^*\psi_2(x)\,dx$$

$$= i\hbar\int_{-\infty}^{\infty}\frac{d\psi_1^*(x)}{dx}\psi_2(x)\,dx. \tag{ii}$$

From (i) and (ii), $\langle\psi_1|P_x\psi_2\rangle = \langle P_x\psi_1|\psi_2\rangle$

Hence $P_x = -i\hbar\frac{d}{dx}$ is Hermitian. Similar calculation with $A = \frac{d}{dx}$ will give,

$$\langle \psi_1 | A\psi_2 \rangle = -\int_{-\infty}^{\infty} \frac{d\psi_1^*(x)}{dx} \psi_2(x)\, dx$$

and $$\langle A\psi_1 | \psi_2 \rangle = \int_{-\infty}^{\infty} \frac{d\psi_1^*(x)}{dx} \psi_2(x)\, dx .$$

Hence $\langle \psi_1 | A\psi_2 \rangle \neq \langle A\psi_1 | \psi_2 \rangle$ and so, $A = \frac{d}{dx}$ is not Hermitian.

4. Show that $AA^\dagger$ is a Hermitian operator for arbitrary operator A.

Solution: $(AA)^\dagger = \left(A^\dagger\right)^\dagger A^\dagger = AA^\dagger$

Hence $AA^\dagger$ is self adjoint and hence Hermitian.

5. Show that Hermitian adjoint of the operator iA is $-iA^\dagger$.

Solution: Let $\psi_1(x)$ and $\psi_2(x)$ be two arbitrary wave functions.

$$\begin{aligned} \langle \psi_1 | iA\psi_2 \rangle &= \int_{-\infty}^{\infty} \psi_1^*(x)[iA\psi_2(x)]\, dx \\ &= \int_{-\infty}^{\infty} [-i\psi_1(x)]^* [A\psi_2(x)]\, dx \\ &= \int_{-\infty}^{\infty} A^\dagger [-i\psi_1(x)]^* \psi_2(x)\, dx \\ &= \left\langle -iA^\dagger\psi_1 \middle| \psi_2 \right\rangle . \end{aligned}$$

Thus the adjoint of iA is $-iA^\dagger$.

6. Show that $(1+i)AB + (1-i)BA$ is Hermitian if A and B are Hermitian operators.

Solution: $$\begin{aligned} \left[(1+i)AB + (1-i)BA\right]^\dagger &= \left[(1+i)AB\right]^\dagger + \left[(1-i)BA\right]^\dagger \\ &= (1+i)^*(AB)^\dagger + (1-i)^*(BA)^\dagger \\ &= (1-i)B^\dagger A^\dagger + (1+i)A^\dagger B^\dagger \\ &= (1-i)BA + (1+i)AB \\ &= (1+i)AB + (1-i)BA \end{aligned}$$

Thus the given operator is Hermitian.

7. Show that $\left(A^n\right)^\dagger = \left(A^\dagger\right)^n$ where A is a operator and n is a positive integer.

Solution: Let me use the method of mathematical induction. The statement $\left(A^n\right)^\dagger = \left(A^\dagger\right)^n$ is obviously true for $n = 1$. Let it be true for some value r of n. Then,

$$\left(A^r\right)^\dagger = \left(A^\dagger\right)^r .$$

Now, $$\left(A^{r+1}\right)^\dagger = \left(A^r . A\right)^\dagger$$

$$= A^{\dagger}\left(A^{\dagger}\right)^{r} = \left(A^{\dagger}\right)^{r+1}.$$

This means, the statement is also true for $r+1$. As it is true for $n=1$, it must be true for $n=2$. But if it true for $n=2$, it must be true for $n=3$ and so on. So the statement is true for all positive integral values of n.

8. Show that $\left[X^{n}, P_x\right] = in\hbar X^{n-1}$ for all positive integral values of n.

Solution: I will prove the above by the method of induction. If I put $n = 1$, the given equation is

$$[X, P_x] = i\hbar$$

which is true. Now suppose it is true for a particular value r of n. Then

$$\left[X^{r}, P_x\right] = ir\hbar X^{r-1}.$$

Now
$$\left[X^{r+1}, P_x\right] = \left[XX^{r}, P_x\right]$$
$$= X\left[X^{r}, P_x\right] + [X, P_x]X^{r}$$
$$= X\left(ir\hbar X^{r-1}\right) + i\hbar X^{r}$$
$$= i(r+1)\hbar X^{r}.$$

Thus if the equation is true for $n = r$, it is also true for $n = r+1$. But it is true for $n = 1$. So it is true for $n = 2$ and hence for $n = 3$ and hence for $n = 4$ and so on. Thus it is true for all positive integral values of n.

9. Prove that $[XP_x, H] = \frac{i\hbar}{m}P_x^2 + X[P_x, V]$ where $H = \frac{P_x^2}{2m} + V$, and V is potential energy operator

Solution:
$$[XP_x, H] = X[P_x, H] + [X, H]P_x$$
$$= X\left[P_x, \frac{P_x^2}{2m} + V\right] + \left[X, \frac{P_x^2}{2m} + V\right]P_x$$
$$= X\left[P_x, \frac{P_x^2}{2m}\right] + X[P_x, V] + \left[X, \frac{P_x^2}{2m}\right]P_x + [X, V]P_x$$

The potential energy operator is assumed to be multiplication by a function of x. Thus the last commutator is zero. Also the first commutator is zero. Thus,

$$[XP_x, H] = X[P_x, V] + \left[X, \frac{P_x^2}{2m}\right]P_x$$
$$= X[P_x, V] + \frac{1}{2m}\left[X, P_x^2\right]P_x$$
$$= X[P_x, V] + \frac{1}{2m}\left\{P_x\left[X, P_x\right] + \left[X, P_x\right]P_x\right\}P_x$$
$$= X[P_x, V] + \frac{1}{2m}(2i\hbar P_x)P_x$$
$$= \frac{i\hbar}{m}P_x^{\,2} + X[P_x, V].$$

EXERCISES

1. Let $\psi(x) = Ae^{-\frac{x^2}{a^2}}e^{\frac{i}{\hbar}p_0x}$. Calculate $XP_X\psi$ and $P_XX\psi$. **Ans.** $x\left(\frac{2i\hbar x}{a^2}+p_0\right)\psi$, $-i\hbar\psi + x\left(\frac{2i\hbar x}{a^2}+p_0\right)\psi$

2. Which of the following operators are linear? (a) $A\,f(x) = XP_X^2\,f(x)$, (b) $B\,f(x) = f(x)P_X\,f(x)$. **Ans.** A

3. Let $|\phi\rangle$ be an eigenstate of A with eigenvalue a. Show that it is also an eigenstate of A^2 and find the corresponding eigenvalue. **Ans.** a^2

4. Let A and B be two Hermitain operators. Is AB necessarily Hermitian? Is ABA necessarily Hermitian? **Ans.** No, yes

5. Let A be the operator "multiplication by x" and B be the operator "differentiation with respect to x". Is A Hermitian? Is B Hermitian? (b) What is $AB\,f(x) - BA\,f(x)$? **Ans.** (a) Yes, No (b) $f(x)$

6. Idendity operator I acting on a function leaves it unchanged. What are the eigen values of I? What are the eigenfunctions? What is the degeneracy of the eigenvalue (s)? **Ans.** 1, all functions, infinity

7. Prove that the Hermitian adjoint of $X + \frac{i}{\hbar}P_X$ is $X - \frac{i}{\hbar}P_X$.

8. What is the Hermitian adjoint of the operator $-i\hbar\frac{d}{dx}$? **Ans.** $-i\hbar\frac{d}{dx}$

9. Find the Hermitian adjoint of the operator $\hbar\frac{d}{dx}$. **Ans.** $-\hbar\frac{d}{dx}$

10. Write the Hermitial adjoint of $(1+i)AB + (2+i)BC + (3+i)CA$.

Ans. $(1-i)B^{\dagger}A^{\dagger} + (2-i)C^{\dagger}B^{\dagger} + (3-i)A^{\dagger}C^{\dagger}$

11. Let A and B be two operators and $|\alpha\rangle, |\beta\rangle$ be two state vectors with the following relations, $A|\alpha\rangle = i|\beta\rangle$, $A|\beta\rangle = -i|\alpha\rangle$, $B|\alpha\rangle = -i|\beta\rangle$, $B|\beta\rangle, = i|\alpha\rangle$.

Find $AB|\alpha\rangle$ and $AB|\beta\rangle$. **Ans.** $-|\alpha\rangle, -|\beta\rangle$

12. Write the Hermitian adjoint of $\left(A+A^2\right)\left(B+B^2\right)$ if A, B are Hermitian operators. **Ans.** $\left(B+B^2\right)\left(A+A^2\right)$

13. Write the Hermitial adjoint of $(1+A)\left(1+A+A^2\right)$ if Hermitian adjoint of A is B. **Ans.** $(1+B)\left(1+B+B^2\right)$

14. Let $\psi_1(x) = \left(\frac{2}{a^2\pi}\right)^{1/4}e^{-x^2/a^2}$ and $\psi_2(x) = \left(\frac{32}{a^6\pi}\right)^{1/4}xe^{-x^2/a^2}$. Calculate $\langle\psi_2|P_X|\psi_1\rangle$. **Ans.** $\frac{i\hbar}{a}$

15. Show that $[AB, C] = B[A, C] + [A, C]B$.

16. Simplify the expressions $[X, P_X^2]$ and $[X^2, P_X]$. **Ans.** $2i\hbar P_X$, $2i\hbar X$

17. Calculate (a) $[XP_X + P_XX, X]$ (b) $[XP_X + P_XX, P_X]$ **Ans.(a)** $-2i\hbar X$ **(b)** $2i\hbar P_X$

18. Consider the operator $H = K + V$ where $K = \frac{P_X^2}{2m}$ and $V = \frac{1}{2}m\omega^2X^2$. Verify that $[H, K] = -[H, V] = -[K, V]$ and get its expression in terms of X and P_X. **Ans.** $\frac{i\hbar\omega^2}{2}(XP_X + P_XX)$

19. Show that if A and B are Hermitian and $[A, B] = 0$, AB is also a Hermitian operator.

20. Show that $(ABC)^\dagger = C^\dagger B^\dagger A^\dagger$.

21. Which of the following are surely correct for two Hermitian operators A and B?

(a) $(AB)^\dagger = AB$ (b) $(AB)^\dagger = A^\dagger B^\dagger$ (c) $(AB)^\dagger = BA$ (d) $(AB)^\dagger = B^\dagger A^\dagger$

Ans. (c) and (d)

22. Prove that $i[A,B]$ is a Hermitian operator if A, B are themselves Hermitain.

23. Certain expressions are suggested for $(A+B)^2 f(x)$ where A and B are operators. Which of these are correct?

(a) $\left[(A+B)f(x)\right]^2$

(b) $A^2 f(x) + B^2 f(x) + 2AB\, f(x)$

(c) $A^2 f(x) + B^2 f(x) + AB\, f(x) + BA\, f(x)$

(d) $A^2 f(x) + B^2 f(x) + A f(x) B\, f(x)$.

Ans. (c)

8

More on Operators—Operator Formulation III

Eigenvalues and eigenfunctions of Hermitian operators are very important for a quantum physicist. These are directly related to the possible results of measurement of physical quantities and probabilities of getting these results. I will therefore devote this chapter on the mathematical properties of Hermitian operators, their eigenvalues and their eigenfunctions. Some other useful operators will also be on the agenda.

8.1 Eigenvalues of a Hermitian operator are real

Let A be a Hermitian operator and $\phi(x)$ be an eigenfunction of A with eigenvalue a. This means

$$A\phi(x) = a\,\phi(x).$$

Operation of A on $\phi(x)$ gives the same function $\phi(x)$ except for an overall multiplication by a pure number a. Writing $\phi(x)$ as $|\phi\rangle$, the above equation becomes,

$$A\,|\phi\rangle = a\,|\phi\rangle. \tag{i}$$

Take scalar product of each side of this equation with $|\phi\rangle$. This gives,

$$\langle\phi|A|\phi\rangle = a\langle\phi|\phi\rangle. \tag{ii}$$

I have written a outside the scalar product $\langle\phi|\phi\rangle$. This is because the scalar product is an integration on x and a is a pure number which can be taken out of the integration. Now take complex conjugate of each side of (ii). You get

$$\langle\phi|A|\phi\rangle^* = a^*\langle\phi|\phi\rangle^*. \tag{iii}$$

But $$\langle\phi|\phi\rangle = \int_{-\infty}^{\infty}\phi^*(x)\,\phi(x)\,dx = \int_{-\infty}^{\infty}|\phi(x)|^2\,dx.$$

Hence it has to be real (and also positive). Hence $\langle\phi|\phi\rangle^* = \langle\phi|\phi\rangle$. Also A is a Hermitian operator and for any Hermitian operator

$$\langle\psi_1|A|\psi_2\rangle^* = \langle\psi_2|A|\psi_1\rangle.$$

Thus $$\langle\phi|A|\phi\rangle^* = \langle\phi|A|\phi\rangle.$$

Equation (iii), therefore, can be written as

$$\langle\phi|A|\phi\rangle = a^*\langle\phi|\phi\rangle.$$

Comparing with (ii),

$$a\langle\phi|\phi\rangle = a^*\langle\phi|\phi\rangle$$

or, $$(a - a^*)\langle\phi|\phi\rangle = 0.$$

As $\langle\phi|\phi\rangle$ is not zero, you get $a = a^*$. This proves that a is real. Thus all eigenvalues of a Hermitian operator are real.

8.2 Eigenfunctions of a Hermitian operator corresponding to different eigenvalues are orthogonal to each other

Suppose $|\phi_1\rangle$ and $|\phi_2\rangle$ are two eigenfunctions of a Hermitian operator A with different eigenvalues a_1 and a_2. Thus,

$$A|\phi_1\rangle = a_1|\phi_1\rangle \quad \text{(i)}$$

and

$$A|\phi_2\rangle = a_2|\phi_2\rangle \quad \text{(ii)}$$

with $a_1 \neq a_2$. I will show that $\langle\phi_1|\phi_2\rangle = 0$.

Take scalar product of each side of (i) with $|\phi_2\rangle$, and of each side of (ii) with $|\phi_1\rangle$.

$$\langle\phi_2|A|\phi_1\rangle = a_1\langle\phi_2|\phi_1\rangle \quad \text{(iii)}$$

$$\langle\phi_1|A|\phi_2\rangle = a_2\langle\phi_1|\phi_2\rangle. \quad \text{(iv)}$$

Take complex conjugates of each side of equation (iii). This gives,

$$\langle\phi_2|A|\phi_1\rangle^* = a_1^*\langle\phi_2|\phi_1\rangle^*. \quad \text{(v)}$$

But $\langle\phi_2|A|\phi_1\rangle^* = \langle\phi_1|A|\phi_2\rangle$ (as A is Hermitian)

$\langle\phi_2|\phi_1\rangle^* = \langle\phi_1|\phi_2\rangle$ (definition of scalar product)

and $a_1^* = a_1$. (eigenvalues of a Hermitian operator are real).

So, (v) becomes

$$\langle\phi_1|A|\phi_2\rangle = a_1\langle\phi_1|\phi_2\rangle.$$

Compare with equation (iv)

$$a_2\langle\phi_1|\phi_2\rangle = a_1\langle\phi_1|\phi_2\rangle$$

or

$$(a_2 - a_1)\langle\phi_1|\phi_2\rangle = 0.$$

As we started with the assumption that $a_1 \neq a_2$ this equation tells that $\langle\phi_1|\phi_2\rangle = 0$, that is, $|\phi_1\rangle$ and $|\phi_2\rangle$ are orthogonal to each other.

8.3 Degenerate eigenvalues

Let $|\phi\rangle$ be an eigenfunction of A with eigenvalue a. So,

$$A|\phi\rangle = a|\phi\rangle.$$

For any constant c,

$$A(c|\phi\rangle) = c(A|\phi\rangle) = c(a|\phi\rangle)$$

or,

$$A(c|\phi\rangle) = a(c|\phi\rangle).$$

But the last result shows that the function $c|\phi\rangle$ is an eigenfunction of A with the same eigenvalue a. So, if you have one eigenfunction $|\phi\rangle$ of A, you can produce infinite number of eigenfunctions of A by just multiplying this $|\phi\rangle$ by different numbers c. However these eigenfunctions are not independent of each other. They are just multiples of each other. In quantum mechanics if a wave function is multiplied by a constant it still represents the same state of the particle. So, all these eigenfunctions $c|\phi\rangle$ are not considered as separate. We pick up one representative eigenfunction out of these (generally a normalized one) and identify that as *the* eigenfunction representing this whole family.

It is possible to have two eigenfunctions of an operator with the same eigenvalue, which are not multiple of each other. For example, consider the kinetic energy operator

$$K = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}.$$

Verify that both sin kx and cos kx are eigenfunctions of this operator with the same eigenvalue $\hbar^2k^2/(2m)$.

$$K(\sin kx) = -\frac{\hbar^2}{2m}\left[\frac{d^2}{dx^2}(\sin kx)\right] = \frac{\hbar^2k^2}{2m}(\sin kx).$$

Similarly, $$K(\cos kx) = \frac{\hbar^2k^2}{2m}(\cos kx).$$

The two functions sin kx and cos kx are independent of each other in the sense that you cannot get one by multiplying the other by a constant. They are genuinely different. Let me define precisely what I mean by independent functions.

A number of functions are called independent if none of these can be written as a linear combination of the rest.

For two functions, this condition is the same as saying that one is not a multiple of other.

If there are two independent eigenfunctions of an operator with the same eigenvalue, the eigenvalue is called *doubly degenerate* or *two-fold degenerate*. In the above example $\hbar^2k^2/(2m)$ is a doubly degenerate eigenvalue of K.

You can check that $K\left(e^{ikx}\right) = \frac{\hbar^2k^2}{2m}e^{ikx}$ So, e^{ikx} is also an eigenfunction of K with the same eigenvalue $\frac{\hbar^2k^2}{2m}$. However $\sin kx, \cos kx$ and e^{ikx} are not independent functions as you can write $e^{ikx} = \cos kx + i\sin kx$.

Let $|\phi_1\rangle$ and $|\phi_2\rangle$ be two independent eigenfunctions of A with the same eigenvalue a. Then,

$$A|\phi_1\rangle = a|\phi_1\rangle$$

and $$A|\phi_2\rangle = a|\phi_2\rangle.$$

Let $|\phi\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle$ be a linear combination of $|\phi_1\rangle$ and $|\phi_2\rangle$. Here c_1 and c_2 are constants. Then,

$$\begin{aligned}
A|\phi\rangle &= A\left[c_1|\phi_1\rangle + c_2|\phi_2\rangle\right] \\
&= A\left[c_1|\phi_1\rangle\right] + A\left[c_2|\phi_2\rangle\right] \\
&= c_1\left[A|\phi_1\rangle\right] + c_2\left[A|\phi_2\rangle\right] \\
&= c_1a|\phi_1\rangle + c_2a|\phi_2\rangle \\
&= a\left[c_1|\phi_1\rangle + c_2|\phi_2\rangle\right] \\
&= a|\phi\rangle.
\end{aligned}$$

So, $|\phi\rangle$ is also an eigenfunction of A with the same eigenvalue a. Thus if there are two independent eigenfunctions $|\phi_1\rangle$ and $|\phi_2\rangle$ of an operator with the same eigenvalue, all possible linear combinations of $|\phi_1\rangle$ and $|\phi_2\rangle$ are also eigenfunctions of the operator with the same eigenvalue. But all these infinite number of eigenfunctions are not independent of each other. You can have only two independent eigenfunctions and any third eigenfunction will be a combination of these two.

In general, if there are n independent eigenfunctions of an operator with the same eigenvalue, this eigenvalue is called *n fold degenerate*. All linear combinations of these n eigenfunctions are also eigenfunctions of this operator with the same eigenvalue. A one-fold degenerate eigenvalue is also called a nondegenerate eigenvalue.

In Section 8.2, it was shown that eigenfunctions corresponding to different eigenvalues are orthogonal to each other. But eigenfunctions corresponding to the same eigenvalue may or may not be orthogonal. If there is an n-fold degenerate eigenvalue, we have infinite number of eigenfunctions corresponding to this eigenvalue (at best n of these are independent) and all these are not orthogonal to each other. But let me assure you that it is always possible to pick up n eigenfunctions out of these infinite number of eigenfunctions, which are orthogonal to each other. When a quantum physicist makes a list of eigenfunctions of an operator he/she tends to select such orthogonal eigenfunctions only.

8.4 Simultaneous eigenfunctions of two commuting operators

Suppose A and B are two commuting operators. Thus AB = BA or $[A, B] = 0$. Suppose A has a nondegenerate eigenvalue a, and the corresponding eigenfunction is $|\phi\rangle$. This means

$$A|\phi\rangle = a|\phi\rangle$$

and there is no other independent eigenfunction of A with this eigenvalue a. Indeed any multiple $c|\phi\rangle$ is also an eigenfunction of A with eigenvalue a, but that is not independent. Now,

$$\begin{aligned}(BA)|\phi\rangle = B\left[A|\phi\rangle\right] &= B\left[a|\phi\rangle\right] \\ &= a\left[B|\phi\rangle\right]. \end{aligned} \tag{i}$$

But A and B commute, so BA = AB. Thus (i) can also be written as,

$$(AB)|\phi\rangle = a[B|\phi\rangle]$$

or

$$A\left[B|\phi\rangle\right] = a\left[B|\phi\rangle\right]. \tag{ii}$$

This equation tells us that $\left[B|\phi\rangle\right]$ is an eigenfunction of A with the eigenvalue a. But we assumed that a is a nondegenerate eigenvalue of A with eigenfunction $|\phi\rangle$ and hence there is no other independent eigenfunction of A with this same eigenvalue. So, $\left[B|\phi\rangle\right]$ must be a multiple of $|\phi\rangle$. In other words,

$$B|\phi\rangle = b|\phi\rangle$$

where b is a constant. But this means, $|\phi\rangle$ is an eigenfunction of B. So, I have proved the following theorem.

If two operators A *and* B *commute, any eigenfunction of* A *corresponding to a nondegenerate eigenvalue is also an eigenfunction of* B.

If all eigenvalues of A are nondegenerate, then all eigenfunctions of A are also eigenfunctions of B. If all the eigenvalues of B are also nondegenerate, all eigenfunctions of the two operators are common.

What happens if an eigenvalue a of A is degenerate? To start with, suppose it is doubly degenerate and $|\phi_1\rangle$ and $|\phi_2\rangle$ are two independent eigenfunctions corresponding to this same eigenvalue. All functions $c_1|\phi_1\rangle + c_2|\phi_2\rangle$ for arbitrary values of c_1 and c_2 are also eigenfunctions of A with the same eigenvalue a. We still have equation (ii) valid for each of the eigenfunctions of A and hence,

$$A\left[B|\phi_1\rangle\right] = a\left[B|\phi_1\rangle\right].$$

So, $B|\phi_1\rangle$ is an eigenfunction of A with eigenvalue a. But we cannot say that $B|\phi_1\rangle$ is a multiple of $|\phi_1\rangle$ because two eigenfunctions of A with a degenerate eigenvalue a may be independent of each other and hence need not be multiple of each other.

So each eigenfunction of A with eigenvalue a need not be an eigenfunction of B. However it turns out that out of the infinite number of eigenfunctions $c_1|\phi_1\rangle + c_2|\phi_2\rangle$, you can choose at least two which are also eigenfunctions of B. To illustrate this, let me consider an example.

You know that the functions sin kx and cos kx are eigenfunctions of the kinetic energy operator K with the same eigenvalue $\hbar^2k^2/(2m)$. The linear momentum operator P_x commutes with K (both are differentiation type). Are sin kx and cos kx also eigenfunctions of P_x?

$$P_x(\sin kx) = \left(-i\hbar\frac{d}{dx}\right)(\sin kx) = -i\hbar k\cos kx .$$

You see, it has not given me a multiple of sin kx. Thus sin kx is not an eigenfunction of P_x, although it is an eigenfunction of K. Similarly cos kx is not an eigenfunction of P_x. However, if you make a linear combination

$$\cos kx + i\sin kx = e^{ikx}$$

it is an eigenfunction of K as well as P_x as shown below.

$$K\,e^{ikx} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}(e^{ikx}) = \frac{\hbar^2k^2}{2m}(e^{ikx})$$

and

$$P_x e^{ikx} = -i\hbar\frac{d}{dx}(e^{ikx}) = \hbar k(e^{ikx}).$$

Another linear combination $\cos kx - i\sin kx = e^{-ikx}$ is also a simultaneous eigenfunction of K and P_x. Thus each eigenfunction of K corresponding to the degenerate eigenvalue $\hbar^2k^2/(2m)$ is not an eigenfunction of P_x, but we can choose two linearly independent functions which are eigenfunctions of K with the eigenvalue $\hbar^2k^2/(2m)$ and are also eigenfunctions of P_x.

In general, if there is an n-fold degenerate eigenvalue of an operator A, and another operator B commutes with it, you can surely get n independent eigenfunctions of A with this eigenvalue which are also eigenfunctions of B. I am not proving it, but you take it from me. If you are interested in writing a set of all independent eigenfunctions of A, you can choose these functions from the simultaneous eigenfunctions of A and B if they commute. We say that there is a complete set of common eigenfunctions of A and B if they commute. If there are more than two operators, all commuting with each other, you have a complete set of common eigenfunctions of all these. Complete set means any function may be written as a linear combination of these.

If A and B are two operators which do not commute, in general, they do not have simultaneous eigenfunctions. For, if they have a simultaneous eigenfunction $|\phi\rangle$,

$$A|\phi\rangle = a|\phi\rangle \text{ and } B|\phi\rangle = b|\phi\rangle .$$

Then,
$$BA|\phi\rangle = Ba|\phi\rangle = aB|\phi\rangle = ab|\phi\rangle$$

and,
$$AB|\phi\rangle = Ab|\phi\rangle = bA|\phi\rangle = ab|\phi\rangle .$$

So,
$$AB|\phi\rangle = BA|\phi\rangle$$

or,
$$[AB - BA]|\phi\rangle = 0 . \qquad \text{(iii)}$$

Thus, A, B can have a simultaneous eigenfunction $|\phi\rangle$ only if the operator AB − BA (which itself is not zero if A and B do not commute) operating on $|\phi\rangle$ gives zero function. There are certain cases where it does happen. But in general, if A and B do not commute, equation (iii) is not satisfied and they do not have simultaneous eigenfunctions. For example, $[X, P_x] = i\hbar$. So, for any function $|\phi\rangle$

$$[XP_x - P_xX]|\phi\rangle = i\hbar|\phi\rangle$$

which is not zero unless $|\phi\rangle$ itself is zero ($\phi(x)=0$ everywhere). That is not a possible wave function any way. So position and momentum operators cannot have any common eigenfunction.

8.5 Basis for the state space in terms of the eigenfunctions of an operator

A set of independent functions $|\phi_1\rangle$, $|\phi_2\rangle$, $|\phi_3\rangle$, ... is called a *basis* for the state space F, if each function in F can be written as a linear combination of these functions (Don't worry about continuous basis, the basic physics in this section is the same for discrete and continuous basis). We generally choose orthonormal basis where the basis vectors are all orthogonal to each other and each of these vectors is normalized. Suppose a is a physically measurable quantity for a particle and A is the corresponding Hermitian operator. Any wave function $|\psi\rangle$ of the particle can be expanded as a linear combination of the eigenfunctions of A (and the coefficients appearing in this expansion are related to the probabilities of getting particular values of a in a measurement). Thus if you just write down the independent eigenfunctions of A, these will form a basis for the state space F.

If all the eigenvalues of the operator A are nondegenerate, the task is simple. Just write the eigenfunctions and you get an orthogonal basis for F. Choose normalized eigenfunctions and you have an orthonormal basis. What happens if an eigenvalue, say a_1, is *n*-fold degenerate? You have to choose a set of *n* orthogonal eigenfunctions of A with the eigenvalue a_1 and include in the basis. But in all cases it is possible to get an orthonormal basis of the state space F from the eigenfunctions of A.

What if you start with a different quantity b for which the Hermitian operator is B. You can again get a basis from the eigenfunctions of B. If A and B commute and all the eigenvalues of A and B are nondegenerate, you end up with the same set of eigenfunctions. If they commute but some of the eigenvalues of are degenerate then each eigenfunction of A is not necessarily an eigenfunction of B, but you can still choose a basis from the simultaneous eigenfunctions of A and B. But if A and B do not commute, you cannot choose a basis from simultaneous eigenfunctions of A and B. This is because in general they do not have simultaneous eigenfunctions and even if they have, they do not have enough simultaneous eigenfunctions to form a basis.

8.6 Some important operators

(a) Projection operator

Suppose $|\phi_i\rangle$, $i = 1, 2, 3, \ldots$ form an orthonormal basis of the state space F. Let me write an expression

$$P_i = |\phi_i\rangle\langle\phi_i|.$$

I can treat this as an operator with the following meaning.

$$\begin{aligned} P_i|\psi\rangle = |\phi_i\rangle\langle\phi_i|\psi\rangle &= \langle\phi_i|\psi\rangle\ |\phi_i\rangle \\ &= \left[\int_{-\infty}^{\infty}\phi_i^*(x)\,\psi(x)\,dx\right]|\phi_i\rangle \\ &= c_i\,|\phi_i\rangle. \end{aligned}$$

When $|\phi_i\rangle\langle\phi_i|$ operates on a function $|\psi\rangle$ it gives a new function which is a multiple of $|\phi_i\rangle$. In fact $c_i = \langle\phi_i|\psi\rangle$ is the component of $|\psi\rangle$ along $|\phi_i\rangle$. In other words, if $|\psi\rangle$ is written in terms of $|\phi_i\rangle$'s $|\psi\rangle = \sum c_i\,\phi_i$ with $c_i = \langle\phi_i|\psi\rangle$. Therefore $P_i = |\phi_i\rangle\langle\phi_i|$ is called a *projection operator*.

The term projection is commonly used in geometrical vector space. The projection of a vector **A** on $\hat{i}$ is $A_x\hat{i}$. Similarly, the projection of $|\psi\rangle$ on $|\phi_i\rangle$ is $c_i\,|\phi_i\rangle$.

What is the operator $\sum_i|\phi_i\rangle\langle\phi_i|$ where the index i runs through all the basis vectors? Operate it on any wave function $|\psi\rangle$. You get,

$$\left[\sum_i |\phi_i\rangle\langle\phi_i|\right]|\psi\rangle = \sum_i |\phi_i\rangle\langle\phi_i|\psi\rangle = \sum_i c_i|\phi_i\rangle = |\psi\rangle .$$

The operator $\sum_i |\phi_i\rangle\langle\phi_i|$ operating on any wave function leaves it unchanged. This is the *unity operator.*

Eigenvalues and eigenfunctions of the Projection operator

Let $|\psi\rangle$ be an eigenfunction of the projection operator $|\phi_i\rangle\langle\phi_i|$ and λ be the corresponding eigenvalue. Thus,

$$[|\phi_i\rangle\langle\phi_i|]|\psi\rangle = \lambda|\psi\rangle$$

or, $$|\phi_i\rangle\langle\phi_i|\psi\rangle = \lambda|\psi\rangle . \qquad \text{(i)}$$

Taking scalar product on both sides with $\langle\phi_i|$

$$\langle\phi_i|\phi_i\rangle\langle\phi_i|\psi\rangle = \lambda\langle\phi_i|\psi\rangle$$

or, $$(1-\lambda)\langle\phi_i|\psi\rangle = 0 .$$

This is possible only in two conditions. Either λ is equal to 1, or $\langle\phi_i|\psi\rangle = 0$. So one eigenvalue of $|\phi_i\rangle\langle\phi_i|$ is 1. In this case, from (i),

$$\langle\phi_i|\psi\rangle|\phi_i\rangle = |\psi\rangle .$$

This means the eigenfunction $|\psi\rangle$ is a multiple of $|\phi_i\rangle$. As all multiples of an eigenfunction are themselves eigenfunctions with the same eigenvalue, and we have to pick up one representative, we can take $|\phi_i\rangle$ to be the eigenfunction corresponding to the eigenvalue 1.

Now look at the other case, that is, $\langle\phi_i|\psi\rangle = 0$. Equation (i) in this case gives

$$\lambda|\psi\rangle = 0 .$$

But $|\psi\rangle$ itself is not the zero function as it represents a possible wave function. So $\lambda = 0$. Thus all functions orthogonal to $|\phi_i\rangle$ are eigenfunctions of $|\phi_i\rangle\langle\phi_i|$ corresponding to the eigenvalue 0.

So the projection operator $|\phi_i\rangle\langle\phi_i|$ has two eigenvalues 1 and 0. The eigenvalue 1 is nondegenerate and the corresponding eigenfunction is $|\phi_i\rangle$. The eigenvalue 0 is degenerate and all functions orthogonal to $|\phi_i\rangle$ are the corresponding eigenfunctions.

Example 8.1

For any projection operator P, show that (a) P is Hermitian (b) $P^2 = P$.

Solution: (a) Let $P = |\phi\rangle\langle\phi|$ where $|\phi\rangle$ is a normalized state vector. Let $|a\rangle$ and $|b\rangle$ be any two state vectors.

$$P|b\rangle = |\phi\rangle\langle\phi|b\rangle$$

or, $$\langle a|(P|b\rangle) = \langle a|\phi\rangle\langle\phi|b\rangle . \qquad \text{(i)}$$

Also, $$\langle a|P = \langle a|\phi\rangle\langle\phi|$$

or $$(\langle a|P)|b\rangle = \langle a|\phi\rangle\langle\phi|b\rangle \qquad \text{(ii)}$$

From (i) and (ii), $\langle a|(P|b\rangle) = (\langle a|P)|b\rangle$. Hence P is Hermitian.

(b) For any state vector $|a\rangle$,

$$P|a\rangle = |\phi\rangle\langle\phi|a\rangle \qquad \text{(iii)}$$

So, $$P^2|a\rangle = P(P|a\rangle) = (|\phi\rangle\langle\phi|)|\phi\rangle\langle\phi|a\rangle$$

$$= |\phi\rangle\langle\phi|\phi\rangle\langle\phi|a\rangle$$

$$= |\phi\rangle\langle\phi|a\rangle \qquad \text{(iv)}$$

Thus from (iii) and (iv) $P^2|a\rangle = P|a\rangle$.

As $|a\rangle$ is arbitrary state vector, $P^2 = P$.

The two properties proved above in Example 8.1, namely, P is Hermitian and $P^2 = P$, are sometimes taken as the defining properties of a projection operator. Any operator satisfying these operators is called projection operator.

(b) Parity operator

The parity operator operating on a function $\psi(x)$ gives another function which is obtained by replacing x by $-x$ in $\psi(x)$. Thus if Π is the parity operator,

$$\Pi\psi(x) = \psi(-x).$$

For example, $\Pi e^{kx} = e^{-kx}$, $\Pi\cos(kx) = \cos(-kx) = \cos(kx)$, $\Pi\sin(kx) = \sin(-kx) = -\sin(kx)$ etc.

Eigenvalues and eigenfunctions of the parity operator

Let $\phi(x)$ be an eigenfunction of the parity operator Π with the eigenvalue λ. Then

$$\Pi\phi(x) = \lambda\phi(x).$$

Now, $$\Pi[\Pi\phi(x)] = \Pi[\lambda\phi(x)] = \lambda[\Pi\phi(x)] = \lambda^2\phi(x).$$

Also, $$\Pi[\Pi\phi(x)] = \Pi[\phi(-x)] = \phi(x).$$

So, $$\lambda^2\phi(x) = \phi(x)$$

or, $$\lambda^2 = 1$$

or, $$\lambda = +1, -1.$$

There are only two eigenvalues of the parity operator, +1 and −1. For eigenfunctions corresponding to the eigenvalue +1,

$$\Pi\phi(x) = \phi(x)$$

or, $$\phi(-x) = \phi(x).$$

Such a function is called an *even function*. It is symmetric about $x = 0$. Functions like cos kx, e^{-x^2/a^2}, $\frac{1}{x^2 + a^2}$, etc., are even functions. All even functions are eigenfunctions of Π with the same eigenvalue +1. Parity of the state of a particle with an even wave function is said to be +1.

For eigenfunctions of the parity operator corresponding to the eigenvalue −1,

$$\Pi\phi(x) = (-1)\phi(x)$$

or $$\phi(-x) = -\phi(x).$$

Such a function is called an *odd function*. It is antisymmetric about $x = 0$. Functions like $\sin x$ etc are odd. All odd functions of x are eigenfunctions of Π with eigenvalue -1. Parity of the state of a particle with an odd wave function is said to be -1.

There are functions which are neither even nor odd. $e^{x/a}$ is such a function. Check that if you change x to $-x$, you neither get $e^{x/a}$ back nor negative of it. The parity is not definite for this function. you can write

$$e^{x/a} = \left(\frac{e^{x/a} + e^{-x/a}}{2}\right) + \left(\frac{e^{x/a} - e^{-x/a}}{2}\right).$$

The first part is an even function with parity $+1$ and the second part is an odd function with parity -1. So the function $e^{x/a}$ is itself not an eigenfunction of the parity operator Π, but it can be expressed as a linear combination of eigenfunctions of Π.

8.7 Expansion of a wave function in terms of eigenfunctions of an operator

Let a be a dynamical variable and A be the corresponding Hermitian operator. Let the eigenvalues of A be denoted by a_i. Some of these eigenvalues may be degenerate. If a_i is a nondegenerate eigenvalue, I denote the corresponding normalized eigenfunction by $|\phi_i\rangle$. If a_i is a degenerate eigenvalue having degeneracy n_i, I denote the n_i orthonormal eigenfunctions corresponding to it as $|\phi_i^j\rangle$ where j takes values 1, 2, 3, ..., n_i. For example, suppose the eigenvalues a_1, a_2 are nondegenerate, a_3 is doubly degenerate, a_4 is nondegenerate, and so on. The orthonormal eigenfunctions will be written as $|\phi_1\rangle, |\phi_2\rangle, |\phi_3^1\rangle, |\phi_3^2\rangle, |\phi_4\rangle$, etc.

Suppose the wave function of the particle at a given instant is $|\psi\rangle$. This wave function can be written in terms of the eigenfunctions of A as

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle + \sum_i \sum_{j=1}^{n_i} c_{ij} |\phi_i^j\rangle .$$

Here the summation in the first term is over all the nondegenerate eigenvalues and in the second term is over all the degenerate eigenvalues.

Suppose I wish to measure the value of a in this state. What is the probability of getting the value a_i in this measurement? If this eigenvalue is nondegenerate, the probability is given by,

$$P_i = |c_i|^2 . \tag{8.1}$$

If a_i is degenerate, it is given by,

$$P_i = \sum_{j=1}^{n_i} |c_{ij}|^2 . \tag{8.2}$$

So, the expansion coefficients in the expansion of the wave function in terms of eigenfunctions of A give the probabilities of finding different values of a in a measurement.

8.8 Expectation value of a dynamical variable

Suppose there is a dynamical variable a and the corresponding Hermitian operator is A. The eigenfunctions of A are $|\phi_i\rangle$ with eigenvalues a_i. Assume that all eigenvalues of A are nondegenerate. Suppose the wave function of the particle at a given time is $|\psi\rangle$. One can write

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle$$

where $c_i = \langle \phi_i | \psi \rangle$.

The probability of getting a value a_i in a measurement of a is $P_i = |\langle \phi_i | \psi \rangle|^2$ and hence the expectation value of a when the wave function is $|\psi\rangle$ is

$$\langle a \rangle = \sum_i a_i P_i = \sum_i a_i |\langle \phi_i | \psi \rangle|^2 . \tag{i}$$

Now,

$$A|\psi\rangle = A\sum_i c_i |\phi_i\rangle = \sum_i c_i \, A|\phi_i\rangle = \sum_i c_i \, a_i |\phi_i\rangle .$$

Thus,

$$\begin{aligned}\langle \psi | A | \psi \rangle = \langle \psi | \left(\sum_i c_i a_i |\phi_i\rangle \right) &= \sum_i c_i \, a_i \langle \psi | \phi_i \rangle \\ &= \sum_i a_i \langle \phi_i | \psi \rangle \langle \psi | \phi_i \rangle \\ &= \sum_i a_i \langle \phi_i | \psi \rangle \langle \phi_i | \psi \rangle^* = \sum_i a_i |\langle \phi_i | \psi \rangle|^2 .\end{aligned}$$

Using (i),

$$\langle a \rangle = \langle \psi | A | \psi \rangle . \tag{8.3}$$

This gives the expectation value of the variable a. I proved this result assuming that all eigenvalues of A are nondegenerate. This was done only for simplicity. With little more algebra you can prove the above result for the case where some of the eigenvalues are degenerate. This result is true even if the eigenvalues are continuous and not discrete as assumed in the derivation. We have already used such relations for $\langle x \rangle$ and $\langle p_x \rangle$. Now you know that such a relation is valid for any physically measurable quantity (dynamic variable). The quantity $\langle \psi | A | \psi \rangle$ is also written as $\langle A \rangle$.

8.9 You learned in this chapter

- Eigenvalues of a Hermitian operator are real and eigenfunctions corresponding to different eigenvalues are orthogonal.
- An eigenvalue is called n-fold degenerate if there are just n independent eigenfunctions with this eigenvalue. A one-fold degenerate eigenvalue is also called nondegenerate eigenvalue.
- If two operators commute then any eigenfunction of one operator corresponding to a nondegenerate eigenvalue is also an eigenfunction of the other.
- If two operators A and B commute and an eigenvalue of A is n-fold degenerate, it is always possible to find n independent eigenfunctions of A with this eigenvalue, which are also eigenfunctions of B. If two operators A and B commute, one can find a basis of the state space from the simultaneous eigenfunctions of A and B.
- If two operators do not commute, they, in general, do not have simultaneous eigenfunctions. No basis of the state space can be formed from the simultaneous eigenfunctions even if some exist.
- For any given function $|\phi\rangle$ one can construct the projection operator $|\phi\rangle\langle\phi|$. This operator has eigenvalues 0 and 1.
- Parity operator operating on a function $\psi(x)$ changes each x to $-x$ in the function. All even functions are eigenfunctions of parity operator with eigenvalue +1 and all odd functions are eigenfunctions of parity operator with eigenvalue –1.
- The expectation value of a dynamical variable a when the particle is in a state described by the wave function $\psi(x)$, is $\langle \psi | A | \psi \rangle$ where A is the Hermitian operator corresponding to a.

Solved Problems

1. Let $|\phi_m\rangle$ and $|\phi_n\rangle$ represent two wave functions in the state space. Show that the Hermitian adjoint of $|\phi_n\rangle\langle\phi_m|$ is $|\phi_m\rangle\langle\phi_n|$.

Solution: Let $|\psi_1\rangle$ and $|\psi_2\rangle$ be any two wave functions. Let $A = |\phi_n\rangle\langle\phi_m|$ and $B = |\phi_m\rangle\langle\phi_n|$. Then,

$$A|\psi_2\rangle = |\phi_n\rangle\langle\phi_m|\psi_2\rangle$$

or

$$\langle\psi_1|A\psi_2\rangle = \langle\psi_1|\phi_n\rangle\langle\phi_m|\psi_2\rangle. \qquad \text{(i)}$$

Also,

$$B|\psi_1\rangle = |\phi_m\rangle\langle\phi_n||\psi_1\rangle.$$

So,

$$\langle\psi_2|B\psi_1\rangle = \langle\psi_2|\phi_m\rangle\langle\phi_n|\psi_1\rangle.$$

Taking complex conjugates,

$$\langle B\psi_1|\psi_2\rangle = \langle\psi_1|\phi_n\rangle\langle\phi_m|\psi_2\rangle. \qquad \text{(ii)}$$

From (i) and (ii),

$$\langle\psi_1|A\psi_2\rangle = \langle B\psi_1|\psi_2\rangle.$$

Thus, A and B are adjoint of each other and hence the adjoint of $|\phi_n\rangle\langle\phi_m|$ is $|\phi_m\rangle\langle\phi_n|$.

2. Let $|\phi_1\rangle$ and $|\phi_2\rangle$ be two ortonormal state vectors. Let $A = |\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|$. Is A a projection operator?

Solution: For A to be a projection operator, A should be Hermitian and A^2 should be equal to A. The Hermitian adjoint of $|\phi_1\rangle\langle\phi_2|$ is $|\phi_2\rangle\langle\phi_1|$ and that of $|\phi_2\rangle\langle\phi_1|$ is $|\phi_1\rangle\langle\phi_2|$. So

$$\begin{aligned} A^\dagger &= \left[|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|\right]^\dagger \\ &= \left[|\phi_1\rangle\langle\phi_2|\right]^\dagger + \left[|\phi_2\rangle\langle\phi_1|\right]^\dagger \\ &= |\phi_2\rangle\langle\phi_1| + |\phi_1\rangle\langle\phi_2| \\ &= A \end{aligned}$$

Hence A is Hermitian.

Now,

$$\begin{aligned} A^2 &= \left[|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|\right]\left[|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|\right] \\ &= |\phi_1\rangle\langle\phi_2|\left[|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|\right] + |\phi_2\rangle\langle\phi_1|\left[|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|\right] \\ &= \left[|\phi_1\rangle\langle\phi_2|\phi_1\rangle\langle\phi_2| + |\phi_1\rangle\langle\phi_2|\phi_2\rangle\langle\phi_1|\right] + \left[|\phi_2\rangle\langle\phi_1|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|\phi_2\rangle\langle\phi_1|\right] \end{aligned}$$

Since $|\phi_1\rangle$ and $|\phi_2\rangle$ are orthonormal,

$$A^2 = |\phi_1\rangle\langle\phi_1| + |\phi_2\rangle\langle\phi_2|$$

which is not the same as A. So A is not a projection operator.

3. Prove that the parity operator Π is Hermitian.

Solution: Let $|\psi_1\rangle$ and $|\psi_2\rangle$ be arbitrary wave functions.

$$\langle\psi_1|\Pi\psi_2\rangle=\int_{-\infty}^{\infty}\psi_1^*(x)[\Pi\psi_2(x)]dx$$

$$=\int_{-\infty}^{\infty}\psi_1^*(x)\psi_2(-x)dx \qquad \text{(i)}$$

and
$$\langle\Pi\psi_1|\psi_2\rangle=\int_{-\infty}^{\infty}[\Pi\psi_1(x)]^*\psi_2(x)dx$$

$$=\int_{-\infty}^{\infty}\psi_1^*(-x)\psi_2(x)dx\,.$$

Let $y=-x$. Then $dx=-dy$. When $x=-\infty$, $y=+\infty$ and when $x=+\infty$, $y=-\infty$. The above integration becomes,

$$\int_{+\infty}^{-\infty}\psi_1^*(y)\psi_2(-y)(-dy)=-\int_{+\infty}^{-\infty}\psi_1^*(y)\psi_2(-y)\,dy$$

$$=\int_{-\infty}^{\infty}\psi_1^*(y)\psi_2(-y)\,dy\,. \qquad \text{(ii)}$$

The integrations in (i) and (ii) are definite integrations and hence the notation of the variable does not make a difference. Thus

$$\langle\psi_1|\Pi\psi_2\rangle=\langle\Pi\psi_1|\psi_2\rangle$$

showing that Π is Hermitian.

4. Prove that for any wave function $|\phi\rangle$, $\langle\phi|A|\phi\rangle\geq 0$ where A is a projection operator.

Solution: The projection operator A may be written as $|\alpha\rangle\langle\alpha|$ for a particular $|\alpha\rangle$.

$$\langle\phi|A|\phi\rangle=\langle\phi|\alpha\rangle\langle\alpha|\phi\rangle$$

$$=\langle\phi|\alpha\rangle\langle\phi|\alpha\rangle^*$$

$$=|\langle\phi|\alpha\rangle|^2$$

which is always greater than or equal to zero.

5. Let $P_1=|\phi_1\rangle\langle\phi_1|$ and $P_2=|\phi_2\rangle\langle\phi_2|$ be two projection operators where $|\phi_1\rangle$ and $|\phi_2\rangle$ are two independent normalized, but not orthogonal state vectors. Show that $[P_1,P_2]\neq 0$.

Solution: Let $|\alpha\rangle$ be any arbitrary state vector.

$$P_1P_2|\alpha\rangle=|\phi_1\rangle\langle\phi_1|\phi_2\rangle\langle\phi_2|\alpha\rangle$$

and
$$P_2P_1|\alpha\rangle=|\phi_2\rangle\langle\phi_2|\phi_1\rangle\langle\phi_1|\alpha\rangle$$

If
$$[P_1,P_2]=0,\ P_1P_2|\alpha\rangle=P_2P_1|\alpha\rangle$$

or,
$$\langle\phi_1|\phi_2\rangle\langle\phi_2|\alpha\rangle|\phi_1\rangle=\langle\phi_2|\phi_1\rangle\langle\phi_1|\alpha\rangle|\phi_2\rangle$$

or,
$$|\phi_1\rangle=\frac{\langle\phi_2|\phi_1\rangle}{\langle\phi_1|\phi_2\rangle}\frac{\langle\phi_1|\alpha\rangle}{\langle\phi_2|\alpha\rangle}|\phi_2\rangle$$

$$=c|\phi_2\rangle\,.$$

But $|\phi_1\rangle, |\phi_2\rangle$ are given to be independent and hence one can not be written as a multiple of other. Thus $[P_1, P_2] \neq 0$.

Note that $\langle\phi_1|\phi_2\rangle \neq 0$ as given in the question. So I could divide by this quantity in the calculation. If $\langle\phi_1|\phi_2\rangle = 0$ then both P_1P_2 and P_2P_1 are zero operators and hence they are zero.

I also divided by $\langle\phi_2|\alpha\rangle$. As $|\alpha\rangle$ is arbitrary this is ok.

6. Let $A|\psi\rangle = c|\xi\rangle$ and A be a Hermitian operator. Prove that $\langle\psi|AB|\phi\rangle = c^*\langle\xi|B|\phi\rangle$.

Solution: $A|\psi\rangle = e|\xi\rangle$

or, $\langle\psi|A^\dagger = e^*\langle\xi|$

or, $\langle\psi|A = e^*\langle\xi|$

or, $\langle\psi|AB|\phi\rangle = e^*\langle\xi|B|\phi\rangle$.

7. Let $|\phi\rangle$ be a normalizable eigenfunction of the operator $H = \frac{P_x^2}{2m} + V(x)$. Show that the expectation value of P_x in the state $|\phi\rangle$ is zero.

Solution: We have $[X, H] = [X, \frac{P_x^2}{2m} + V(x)]$

$$= [X, \frac{P_x^2}{2m}] + [X, V(x)] = \frac{1}{2m}[X, P_x^2].$$

Using $[A, BC] = B[A, C] + [A, B]C$, this becomes,

$$\frac{1}{2m}(P_x[X, P_x] + [X, P_x]P_x) = \frac{i\hbar}{m}P_x.$$

So, $\frac{i\hbar}{m}P_x = [X, H] = XH - HX$

or $P_x = \frac{m}{i\hbar}(XH - HX)$.

The expectation value of P_x in the state $|\phi\rangle$ is

$$\langle\phi|P_x|\phi\rangle = \frac{m}{i\hbar}\langle\phi|XH - HX|\phi\rangle$$

$$= \frac{m}{i\hbar}\left[\langle\phi|XH|\phi\rangle - \langle\phi|HX|\phi\rangle\right] \qquad \text{(i)}$$

$$= \frac{m}{i\hbar}\left[E\langle\phi|X|\phi\rangle - E\langle\phi|X|\phi\rangle\right] = 0. \qquad \text{(ii)}$$

Here E is the eigenvalue of H corresponding to the eigenfunction $|\phi\rangle$. Note how E is taken out in the two terms in equation (ii). In the first term in the square bracket in equation (i), H is operated on $|\phi\rangle$ on the right, whereas, in the second term H is operated on $\langle\phi|$ on the left. In fact in this step we should have brought E^* out. But H is a Hermitian operator and so the eigenvalue E is real. Hence $E^* = E$.

8. Let $|\phi_i\rangle, i = 1, 2, 3, \ldots$ be an orthonormal basis for the state space and $|\psi_1\rangle$ and $|\psi_2\rangle$ be two orthogonal wave functions. What is the value of $\sum_i \langle\psi_1|\phi_i\rangle\langle\phi_i|\psi_2\rangle$? The index *i* runs over all the basis vectors.

Solution: You can take $|\psi_1\rangle$ and $|\psi_2\rangle$ out of the summation in the given expression, as these do not depend on *i*. Thus the given expression is,

$$I = \langle\psi_1\left[\sum_i |\phi_i\rangle\langle\phi_i|\right]|\psi_2\rangle .$$

But $\sum_i |\phi_i\rangle\langle\phi_i|$ is the same as the unity operator. So,

$$I = \langle\psi_1|\psi_2\rangle = 0$$

as $|\psi_1\rangle$ and $|\psi_2\rangle$ are orthogonal.

9. Prove that $\langle\phi_m|X^2|\phi_m\rangle = \sum_k |\langle\phi_m|X|\phi_k\rangle|^2$ where $|\phi_i\rangle$ denotes a basis state and *k* runs over all such states forming an orthonormal basis.

Solution: The LHS of the given equation is

$$\langle\phi_m|X^2|\phi_m\rangle = \langle\phi_m|XX|\phi_m\rangle$$

$$= \langle\phi_m|\left\langle X\left(\sum_k |\phi_k\rangle\langle\phi_k|\right)X|\phi_m\rangle\right\rangle .$$

This is because $\sum_k |\phi_k\rangle\langle\phi_k|$ is the same as the unity operator. So, the LHS

$$= \sum_k \langle\phi_m|X|\phi_k\rangle\langle\phi_k|X|\phi_m\rangle = \sum_k \left[\langle\phi_m|X|\phi_k\rangle\right]\left[\langle\phi_m|X|\phi_k\rangle^*\right]$$

$$= \sum_k |\langle\phi_m|X|\phi_k\rangle|^2$$

which is the RHS.

10. Consider a two dimensional state space of a quantum system with $|e_1\rangle$ and $|e_2\rangle$ as the orthonormal basis vectors. A Hermitian operator A satisfies the following.

$$\langle e_1|A|e_1\rangle = 0, \langle e_1|A|e_2\rangle = i, \langle e_2|A|e_1\rangle = i, \langle e_2\rangle = 0 .$$

Find $A|e_1\rangle$ and $A|e_2\rangle$ in terms of the basis vectors.

Solution: Let $|\psi\rangle = A|e_1\rangle$. Any state vector in this state space can be written as a linear combination of the basis vectors $|e_1\rangle$ and $|e_2\rangle$. Let $|\psi\rangle = c_1|e_1\rangle + c_2|e_2\rangle$

Then, $c_1 = \langle e_1|\psi\rangle$ and $c_2 = \langle e_2|\psi\rangle$.

So, $c_1 = \langle e_1|\psi\rangle = \langle e_1|A|e_1\rangle = 0$

and $c_2 = \langle e_2|\psi\rangle = \langle e_2|A|e_1\rangle = i$

So, $|\psi\rangle = i|e_2\rangle$ or $A|e_1\rangle = i|e_2\rangle$

Next, suppose $|\phi\rangle = A|e_2\rangle = d_1|e_1\rangle + d_2|e_2\rangle$

Then, $d_1 = \langle e_1|\phi\rangle = \langle e_1|A|e_2\rangle = i$

$$d_2 = \langle e_2|\phi\rangle = \langle e_2|A|e_2\rangle = 0$$

So, $|\phi\rangle = i|e_1\rangle$ or $A|e_2\rangle = i|e_1\rangle$

11. Consider the situation given in the previous problem. Find all eigenvalues and eigenvectors of A.

Solution: Let $c_1|e_1\rangle + c_2|e_2\rangle$ be an eigenvector of A with eigenvalue λ. Then,

$$A\left[c_1|e_1\rangle + c_2|e_2\rangle\right] = \lambda\left[c_1|e_1\rangle + c_2|e_2\rangle\right]$$

Using the results of the previous problem, this equation becomes

$$ic_1|e_2\rangle + ic_2|e_1\rangle = \lambda c_1|e_1\rangle + \lambda c_2|e_2\rangle$$

This gives,

$$ic_1 = \lambda c_2 \text{ and } ic_2 = \lambda c_1 \tag{i}$$

or $(ic_1)(ic_2) = (\lambda c_2)(\lambda c_1)$

or $\lambda^2 = -1$

Note that $c_1 = c_2 = 0$ is other possible solution, but that does not represent a state vector.

Thus, $\lambda = \pm i$.

Thus there are two eigenvalues of A, namely, $+i$ and $-i$.

For $\lambda = +i$, equation (i) gives

$$ic_1 = ic_2$$

or $c_1 = c_2$.

The eigenvector corresponding to the eigenvalue i is therefore $\frac{1}{\sqrt{2}}\left(|e_1\rangle + |e_2\rangle\right)$. I have put $\frac{1}{\sqrt{2}}$ to make this vector normalized. Similarly, the eigenvector corresponding to the eigenvalue $-i$ is $\frac{1}{\sqrt{2}}\left(|e_1\rangle - |e_2\rangle\right)$.

EXERCISES

1. An operator has three eigenvalues, 1, $1+i$ and $1-i$. Is the operator Hermitian? **Ans.** No.
2. A Hermitian operator has two eigenvectors $2|e_1\rangle - 3|e_2\rangle$ and $3|e_1\rangle - 2|e_2\rangle$ and corresponding eigenvalues are λ_1 and λ_2. Is $\lambda_1 = \lambda_2$? Justify your answer. **Ans.** Yes, the given eigenvectors are not orthogonal
3. Let A and B be commuting operators and $|\phi_i\rangle$ denote the eigenfunctions of A. Show that $\langle\phi_i|B|\phi_j\rangle = \delta_{ij}$.
4. Prove that $\langle\phi|[A, B]|\phi\rangle = 0$ where $|\phi\rangle$ is an eigenfunction of the Hermitian operator A, and B is any linear operator.
5. Let $f(x) = e^{-kx}$. Is it an eigenfunction of the linear momentum operator? If yes, what is the corresponding eigenvalue? Is there any conflict with the theorem that the eigenvalues of a Hermitian operator are real? **Ans.** Yes, $i\hbar k$, No
6. Which pairs of operators from X (position), P_x (linear momentum), K (kinetic energy) and $V(x)$ (potential energy), have simultaneous eigenfunctions to form a basis of the state space F? **Ans.** X and $V(x)$, P_x and K

7. Let A be the Hermitian operator corresponding to a dynamical variable a. The wave function $\psi(x)$ at a given time is an eigenfunction of A with eigenvalue a_0. Find the expectation value of a.

Ans. a_0

8. Let $|\phi_1\rangle$ and $|\phi_2\rangle$ denote eigenfunctions of the operator $H = \frac{P_x^2}{2m} + V(x)$ with eigenvalues E_1 and E_2 respectively.

Show that $\langle\phi_1|P_x|\phi_2\rangle = \frac{m(E_2 - E_1)}{i\hbar}\langle\phi_1|X|\phi_2\rangle$.

9. Show that if P is a projection operator, $I - P$ is also a projection operator where I is the identity operator.

10. Let H be an operator having discrete nondegenerate eigenvalues E_n and corresponding eigenvectors $|\phi_n\rangle$ where $n = 1, 2, 3, \ldots$. Show that $H = \sum_n E_n |\phi_n\rangle\langle\phi_n|$.

11. Which of the functions given below are eigenfunctions of the parity operator Π? If a function is an eigenfunction of Π, find the corresponding eigenvalue. If it is not, express it in terms of the eigenfunctions of Π. (a) $\frac{A}{x^2 + a^2}$ (b) $x^2 e^{-\frac{(x-a)^2}{b^2}}$ (c) Axe^{-x^2/a^2} (d) $A(x+a)^2 e^{-x^2/a^2}$

Ans. (a) +1 (c) −1

12. The state space of a system is described by the orthonormal basis vectors $|e_1\rangle$ and $|e_2\rangle$. Consider the operator

$$A = k\left[|e_1\rangle\langle e_1| - i|e_1\rangle\langle e_2| + i|e_2\rangle\langle e_1| - |e_2\rangle\langle e_2|\right]$$

where k is a real constant.

(a) Calculate $A|e_1\rangle$ and $A|e_2\rangle$.

(b) Is A a Hermitian operator?

(c) Find all eigenvalues and eigenvectors of A.

Ans. (a) $k\left[|e_1\rangle + i|e_2\rangle\right], -k\left[i|e_1\rangle + |e_2\rangle\right]$, (b) Yes (c) eigenvalues $\sqrt{2}k$ and $-\sqrt{2}k$, eigenvectors $i|e_1\rangle + \left(1-\sqrt{2}\right)|e_2\rangle$ and $i|e_1\rangle + \left(1+\sqrt{2}\right)|e_2\rangle$

13. Consider a two-dimensional state space of a quantum system with $|e_1\rangle$ and $|e_2\rangle$ as the orthonormal basis vectors. An operator A satisfies $\langle e_1|A|e_1\rangle = \langle e_1|A|e_2\rangle = \langle e_2|A|e_1\rangle = \langle e_2|A|e_2\rangle = 1$ Find $A|e_1\rangle$ and $A|e_2\rangle$.

Ans. $|e_1\rangle + |e_2\rangle$ in both cases

14. Consider the situation given in the above problem. Find all the eigenvalues and eigenvectors of A.

Ans. eigenvalues 0 and 2, eigenvectors $\frac{1}{\sqrt{2}}\left(|e_1\rangle - |e_2\rangle\right)$ and $\frac{1}{\sqrt{2}}\left(|e_1\rangle + |e_2\rangle\right)$

9

As time passes—Schrödinger Equation

So far I have been talking of the wave function of a particle at an instant. That is why I have been writing it as a function of x alone. The emphasis in the previous chapters was on getting information about various measurable quantities at that instant from the wave function $\psi(x)$. The mathematical structure of eigenvalues and eigenfunctions of operators for measurable quantities was developed for this purpose. If you have understood what I have discussed so far, you should be able to tell about the position, momentum, kinetic energy, etc., of a particle at a given instant once the wave function $\psi(x)$ "at that instant" is given to you. So you realize that the wave function $\psi(x)$ contains all the information about the particle that is possible to have at that instant. If its kinetic energy is definite, you know what it is. If it is not, you know the possible values and their probabilities. Similarly for other variables.

Now I wish to address the question how the wave function changes as time passes. If I know the wave function now, how I can get the wave function at a later time.

9.1 Schrödinger equation

What we are looking for is the central task of dynamics. Newton's second law is the basic law of dynamics for classical physics. The "state" of the particle at any instant is described in classical physics by giving its position and velocity at that instant. If these quantities are known at $t = 0$, we can predict their values at any later time by solving the equation

$$m\frac{d^2x}{dt^2} = F(x, t)$$

where $F(x, t)$ is the force on the particle when it is at position x and the time is t. This is Newton's equation and is at the center of the whole of the particle dynamics in classical physics. In quantum mechanics, the basic equation governing the dynamics of a particle is called *Schrödinger equation* and is written as

$$\mathrm{H}|\psi\rangle = i\hbar\frac{\partial}{\partial t}|\psi\rangle. \tag{9.1}$$

Here H is the operator corresponding to the total energy of the system and is given a special name *Hamiltonian* of the system. The wave function $|\psi\rangle$ is treated as a function of space coordinates as well as of time. For a particle in one dimension, this means ψ is a function of x and t. I still have in mind a particle in one dimension. For a conservative system, where the interactions can be expressed as a potential energy function $V(x)$, the total energy is equal to the sum of kinetic energy and potential energy. The Hamiltonian is then,

$$\mathrm{H} = \mathrm{K} + \mathrm{V} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \tag{9.2}$$

The Schrödinger equation is thus,

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x, t) + V(x)\,\psi(x, t) = i\hbar\frac{\partial}{\partial t}\psi(x, t). \tag{9.3}$$

I am using partial derivatives because ψ is now a function of x as well as of t. The generalization to three dimensions is simple. You replace $\dfrac{\partial^2}{\partial x^2}$ with $\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$ and write the wave function as

$\psi(x, y, z, t)$ or $\psi(\mathbf{r}, t)$. The potential energy is also a function of x, y, z or $\mathbf{r}$. The Hamiltonian becomes

$$H = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]+V(\mathbf{r})$$

$$= -\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r}).$$

The symbol ∇^2 is read as "del square". The Schrödinger equation itself becomes

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}, t)+V(\mathbf{r})\psi(\mathbf{r}, t) = i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r}, t). \tag{9.4}$$

I will use this three-dimensional version in later chapters. In this chapter I will continue with one-dimensional case.

How do I derive Schrödinger equation? I will not attempt to do that. I never tried to prove or derive Newton's equations of motion. Seniors told me that this is the equation which gives right answers for balls thrown in air, time period of pendulum, motion of planets and so on. And I believed it. Later when I did some experiments myself I found that yes, the results are indeed as predicted by Newton's laws. Similarly, Schrödinger equation rightly predicts the behavior of atomic transitions, molecular vibrations, semiconductor transistors, and so on, and people believe that it is a fundamental law of nature for quantum systems.

But what made Schrödinger write such an equation which became a fundamental equation, not to be derived from more fundamental equations? This will be an interesting topic for students of history of science. Here I would just show you the simplest chain of arguments which can help one to guess at the Schrödinger equation.

Consider a free particle. The simplest wave function for a free particle one can think of (in one dimension) is

$$\psi(x, t) = A e^{i(kx-\omega t)}. \tag{i}$$

Such a wave is used in many branches of science and engineering. The parameter $k = 2\pi/\lambda$ represents the periodicity of the wave in space and $\omega = 2\pi\nu$ represents its periodicity in time. If it is a wave function for a particle, let us apply de Broglie and Einstein relations.

The de Broglie relation $\lambda = h/p$ gives

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} = \frac{p}{\hbar}$$

and the Einstein equation $E = h\nu$ gives

$$\omega = 2\pi\nu = \frac{2\pi E}{h} = \frac{E}{\hbar}.$$

Putting in (i), $\psi(x, t) = A e^{\frac{i}{\hbar}(px - Et)}$ (ii)

For a free particle, there is no interaction with other objects and hence no potential energy exists. So, $E = \frac{p^2}{2m}$ and equation (ii) becomes

$$\psi(x, t) = Ae^{\frac{i}{\hbar}\left(px-\frac{p^2}{2m}t\right)}. \tag{iii}$$

We started with a specific wave function which may be valid for a specific situation. The wave function in (iii) is one solution of a more general differential equation which allows many more solutions for other situations. So let us try to construct a differential equation of which (iii) is a solution. We can differentiate $\psi(x,t)$ with respect to x and t, once or more and look for the relation between the derivatives.

$$\frac{\partial\psi}{\partial x}=\left(\frac{i}{\hbar}p\right)A\,e^{\frac{i}{\hbar}\left(px-\frac{p^2}{2m}t\right)}$$

$$\frac{\partial^2\psi}{\partial x^2}=\left(\frac{i}{\hbar}p\right)\left(\frac{i}{\hbar}p\right)A\,e^{\frac{i}{\hbar}\left(px-\frac{p^2}{2m}t\right)}\quad=-\frac{p^2}{\hbar^2}A\,e^{\frac{i}{\hbar}\left(px-\frac{p^2}{2m}t\right)}$$

and
$$\frac{\partial\psi}{\partial t}=\left(-\frac{ip^2}{2m\hbar}\right)A\,e^{\frac{i}{\hbar}\left(px-\frac{p^2}{2m}t\right)}.$$

Clearly, $\frac{\partial^2\psi}{\partial x^2}$ and $\frac{\partial\psi}{\partial t}$ are proportional to each other and may be related to get the desired differential equation. You can easily verify that

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}=i\hbar\frac{\partial\psi}{\partial t}. \qquad (iv)$$

For a free particle, $V(x)=0$ so that the Hamiltonian is

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

and equation (iv) is the same as

$$\mathrm{H}\psi=i\hbar\frac{\partial}{\partial t}\psi$$

which is the Schrödinger equation. It needs only a small stretch of imagination to make the assumption that if the particle is subjected to a potential $V(x)$, then also this same equation, with H = K - V, may be used.

9.2 Solving Schrödinger equation

The purpose of Schrödinger equation is to get $\psi(x,t)$ if $\psi(x,0)$ is known. In other words, this equation tells how the wave function of a system evolves as time passes. As written in Equation 9.3, it is a differential equation. Different situations correspond to different expressions for $V(x)$. Once the functional form of $V(x)$ and the initial wave function $\psi(x,0)$ are given, techniques for solving differential equations can be applied to get $\psi(x,t)$. However, Equation 9.3 contains two independent variables x and t and this makes the task somewhat complicated. Fortunately, there is a simple procedure by which you can solve Schrödinger equation more easily.

Write the Hamiltonian H for the given system. This may be in the form of Equation 9.2 with appropriate expression for $V(x)$. Find the normalized eigenfunctions $\phi_i(x)$ and the eigenvalues E_i for this Hamiltonian. This means, solve the equation

$$\mathrm{H}\,\phi(x)=E\,\phi(x). \qquad (9.5)$$

If the eigenvalues are all nondegenerate, well and good. The eigenfunctions $\phi_i(x)$ are orthogonal to each other. If not, choose an orthogonal set of $\phi_i(x)$ from the eigenfunctions. Thus $\phi_i(x)$ form an orthonormal basis for the state space F and any wave function can be expanded as a linear combination of these functions.

Let me use the 'ket' symbols, $|\phi\rangle$ for $\phi(x)$ and so on. Suppose the wave function at $t = 0$ is $|\psi(0)\rangle$. Expand in terms of the basis functions $|\phi_i\rangle$.

$$|\psi(0)\rangle = \sum_i c_i(0)|\phi_i\rangle \qquad \text{(i)}$$

where $c_i(0)$ are the expansion coefficients. Here i runs over all the orthonormal eigenfunctions chosen. I have written 0 in parenthesis to remind that the wave function is written at $t = 0$. You know that,

$$c_i(0) = \langle\phi_i|\psi(0)\rangle .$$

As $|\psi(0)\rangle$ is known (initial wave function is given, we are trying to see how the wave function changes with time), $c_i(0)$'s are also known.

At time t, the wave function has changed to another function which I write as $|\psi(t)\rangle$. This is a different function of x, different from $|\psi(0)\rangle$. But any wave function can be expanded in terms of $|\phi_i\rangle$. You can therefore write

$$|\psi(t)\rangle = \sum_i c_i(t)|\phi_i\rangle . \qquad \text{(ii)}$$

As the function $|\psi(t)\rangle$ is different from $|\psi(0)\rangle$, $c_i(t)$ are also different from $c_i(0)$. You can therefore say that as time passes, the expansion coefficients c_i change. Be absolutely clear that there is no x-dependence in c_i. Any possible x-dependence is only in $|\phi_i\rangle$ which is written for the eigenfunction $\phi_i(x)$.

The Schrödinger equation is,

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \mathrm{H}|\psi(t)\rangle$$

or $$i\hbar\frac{\partial}{\partial t}\left[\sum_i c_i(t)|\phi_i\rangle\right] = \mathrm{H}\sum_i c_i(t)|\phi_i\rangle$$

or $$i\hbar\left[\sum_i \frac{dc_i(t)}{dt}|\phi_i\rangle\right] = \sum_i c_i(t)\,\mathrm{H}|\phi_i\rangle$$

or $$i\hbar\left[\sum_i \frac{dc_i(t)}{dt}|\phi_i\rangle\right] = \sum_i c_i(t)\,E_i\,|\phi_i\rangle$$

or $$\sum_i\left[i\hbar\frac{dc_i}{dt} - c_i(t)E_i\right]|\phi_i\rangle = 0 . \qquad \text{(iii)}$$

In the three-dimensional vector space, if $A_x\hat{\mathbf{i}} + A_y\hat{\mathbf{j}} + A_z\hat{\mathbf{k}} = 0$, we have $A_x = 0$, $A_y = 0$, and $A_z = 0$. Similar is the situation in equation (iii). The functions $|\phi_i\rangle$ are orthogonal basis functions. If the whole expression on the LHS is zero, the expression in the square bracket must be zero for each i separately. So, for each i,

$$i\hbar\frac{dc_i(t)}{dt} - E_i\,c_i(t) = 0$$

or $$\frac{dc_i(t)}{c_i(t)} = -\frac{i}{\hbar}E_i dt$$

or $$\int_{t=0}^{t}\frac{dc_i}{c_i} = -\frac{i}{\hbar}E_i\int_0^t dt$$

or
$$\ln\frac{c_i(t)}{c_i(0)} = -\frac{i}{\hbar}E_i t$$

or
$$c_i(t) = c_i(0)\, e^{-\frac{i}{\hbar}E_i t}.$$

Thus
$$|\psi(t)\rangle = \sum_i c_i(0)\, e^{-\frac{i}{\hbar}E_i t}\,|\phi_i\rangle. \tag{9.6}$$

We have done it. If $|\psi(0)\rangle$ is given, $|\psi(t)\rangle$ is obtained from the above equation. Let me summarize the procedure.

a) Write the Hamiltonian H (operator corresponding to energy) for the given system.

b) Find the eigenvalues E_i and the eigenfunctions $|\phi_i\rangle$, which form an orthonormal basis.

c) Expand the wave function at time $t = 0$ in terms of these basis functions $|\phi_i\rangle$. Get the expansion coefficients $c_i(0)$.

d) Multiply each $c_i(0)$ by the quantity $e^{-\frac{i}{\hbar}E_i t}$. These products are the expansion coefficients for $|\psi(t)\rangle$.

The above prescription is for the case of discrete eigenvalues E_i. If the energy eigenvalues are not discrete, they are not written as E_i but as $E(\lambda)$ where the index λ can vary continuously. The eigenfunctions are likewise written as $\phi(x,\lambda)$ or $|\phi(\lambda)\rangle$. The wave function $|\psi(0)\rangle$ at $t = 0$ is then written as

$$|\psi(0)\rangle = \int c(\lambda, 0)\,|\phi(\lambda)\rangle\, d\lambda$$

where the integration is performed over the full range of λ. The wave function at time t is obtained by multiplying each component $c(\lambda, 0)$ by the quantity $e^{-\frac{i}{\hbar}E(\lambda)t}$.

$$|\psi(t)\rangle = \int c(\lambda, 0)\, e^{-\frac{i}{\hbar}E(\lambda)t}\,|\phi(\lambda)\rangle\, d\lambda. \tag{9.7}$$

Do remember, all these equations describing the time development of the wave function are valid only if no measurement is made between time 0 and t. If you make any measurement on the system in between, you change the wave function abruptly and no one will take responsibility for the failure of the above equations.

9.3 A free particle

Let me give you some practice with writing the wave function at time t if it is known at time $t = 0$. I will choose a simple system, a free particle. Suppose the wave function of a free particle at time $t = 0$ is known to be $\psi(x,0)$. We wish to know its wave function at time t. Let us go step by step.

(a) Write the Hamiltonian

As stated earlier, a free particle means, there are no objects interacting with it and hence its potential energy is zero. The Hamiltonian is therefore the same as the kinetic energy operator. Thus, the Hamiltonian is

$$\mathrm{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}.$$

(b) Find the eigenvalues and eigenfunctions of H forming a basis.

The eigenvalue equation is $H\phi(x) = E\phi(x)$. The solutions $\phi(x)$ are the eigenfunctions and the values of E for which the solutions are found, are the corresponding eigenvalues. Writing the expression for H, the equation is,

$$-\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dt^2} = E\phi(x)$$

or,
$$\frac{d^2\phi(x)}{dt^2} + \frac{2mE}{\hbar^2}\phi(x) = 0 .$$

You know how to solve this equation. There are several different forms in which the solutions may be written. We need an orthonormal set of eigenfunctions. One such set is given by

$$\phi(x, p) = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}px} \tag{9.8}$$

where p can take any value from $-\infty$ to ∞. The corresponding eigenvalues are

$$E(p) = \frac{p^2}{2m} . \tag{9.9}$$

Equations 9.8 and 9.9 give the required eigenfunctions and eigenvalues of H. You must have identified that these functions are momentum eigenfunctions. These form an orthonormal basis.

(c) Expand $\psi(x, 0)$ in terms of the basis functions

You already know how to expand a wave function in terms of the functions given by Equation 9.8. Do it for $\psi(x, 0)$.

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} a(p, 0)\, e^{\frac{i}{\hbar}px}\, dp \tag{i}$$

where,
$$a(p, 0) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} \psi(x, 0)\, e^{-\frac{i}{\hbar}px}\, dx .$$

In (i), $a(p, 0)$ are the expansion coefficients at time $t = 0$.

(d) Write $\psi(x, t)$ from $\psi(x, 0)$

The eigenvalue of the Hamiltonian, corresponding to the eigenfunction $\phi(x, p)$ is $E(p) = p^2/2m$.

Multiply each expansion coefficient $a(p, 0)$ by $e^{-\frac{i}{\hbar}E(p)t}$ in (i). If no measurement is made in between, this gives the wave function at time t. Thus,

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} a(p, 0)\, e^{-\frac{i}{\hbar}\left(\frac{p^2}{2m}\right)t} e^{\frac{i}{\hbar}px}\, dp$$

or,
$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} a(p, 0)\, e^{\frac{i}{\hbar}\left(px - \frac{p^2}{2m}t\right)}\, dp . \tag{9.10}$$

9.3.1 Motion of a wave packet

The wave function $\psi(x,t)$ as given in Equation 9.10 is a superposition of plane waves like $e^{\frac{i}{\hbar}\left(px-\frac{p^2}{2m}t\right)}$ which can be written as $e^{i(kx-\omega t)}$ where, $k=\frac{p}{\hbar}$ and $\omega=\frac{p^2}{2m\hbar}$. This represents a plane wave advancing at a speed

$$v_p=\frac{\omega}{k}=\left(\frac{p^2}{2m\hbar}\right)\Big/\left(\frac{p}{\hbar}\right)=\frac{p}{2m}.$$

If you are still in the classical mind frame, you may identify p/m as the velocity of the particle. But the wave velocity is $p/2m$ and not p/m. The wave velocity cannot be equated to the particle velocity. When I talk of particle velocity, I have in mind a localized entity which changes its location with time at a particular rate. A semi-quantum picture can be thought of, in which the wave function of the particle is in the shape of a narrow wave packet (Figure 9.1). You may mentally think that the particle is located at the center of the wave packet. I said "mentally", because if you tell this to a quantum physicist, he/she will give you a long lecture on why the position of the particle is uncertain and why the center of the wave packet cannot be taken as the location of the particle. But let me continue with the semi-quantum picture. The wave packet as a whole advances a certain distance x in time t and in certain cases you may identify x/t as the particle velocity.

A wave packet is formed by the superposition of a large number of plane waves with different values of p. As time passes each of these plane waves advances with velocity $v_p=p/(2m)$, covering a distance of $pt/(2m)$ in time t. But p is different for different superposing waves and hence they travel different distances in time t. There are two effects of this. The first is that the shape of the wave packet changes with time. If all the waves were advanced by the same distance say x, the superposition would have given the same shape displaced by x. But here different waves cover different distances and hence the superposition gives a different shape. The second effect relates to the velocity of the packet as a whole.

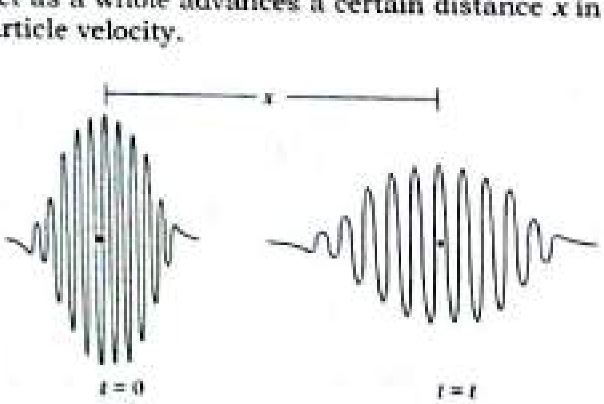


Fig. 9.1

If the wave packet is constructed by superposing waves like $e^{i(kx-\omega t)}$ and the values of k involved are centered around k_0, the wave packet as a whole moves with a velocity

$$v_g=\left.\frac{d\omega}{dk}\right|_{k=k_0}. \tag{9.11}$$

This is called the *group velocity*. The mathematical discussion on this formula is given in Appendix-1. In our case ω and k are given as

$$\omega=\frac{p^2}{2m\hbar}\text{ and }k=\frac{p}{\hbar}$$

giving

$$v_g=\left.\frac{d\omega}{dk}\right|_{k=k_0}$$

$$=\left(\frac{d\omega}{dp}\right)\Big/\left(\frac{dk}{dp}\right)=\left.\frac{p}{m}\right|_{p=p_0}$$

$$=\frac{p_0}{m}$$

where p_0 is the value of linear momentum about which all the momenta corresponding to the superposing waves are centered. This may give some satisfaction that the velocity of the wave packet as a whole, through the space, is in some sense close to what we imagine as the velocity of the particle.

9.3.2 Spreading of Gaussian wave packet

Suppose the wave function of a free particle at time $t = 0$ is given by a Gaussian wave packet

$$\psi(x, 0) = \left(\frac{2}{\pi a^2}\right)^{1/4} e^{-\frac{x^2}{a^2} + \frac{i}{\hbar} p_0 x}.$$

You know that Gaussian wave packets are very special. When a particle has its wave function given by a Gaussian wave packet, the uncertainty product $\Delta x \, \Delta p_x$ has its minimum value $\hbar/2$. Let us see what happens at time t.

Make the standard expansion in terms of $\phi(x, p)$ defined in Equation 9.8 and get the expansion coefficient $a(p, 0)$. We had done it earlier while studying the momentum uncertainty in such a state. Never mind, do it again.

$$a(p, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x, 0)\, e^{-\frac{i}{\hbar} px} dx$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \left(\frac{2}{\pi a^2}\right)^{1/4} \int_{-\infty}^{\infty} e^{-\frac{x^2}{a^2} + \frac{i}{\hbar}(p_0 - p)x} dx$$

$$= \frac{1}{(2\pi)^{1/4}} \sqrt{\frac{a}{\hbar}} \exp\left[-\frac{a^2 (p - p_0)^2}{4\hbar^2}\right]. \qquad \text{(i)}$$

The wave function at $t = 0$ is

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} a(p, 0) \exp\left[\frac{i}{\hbar} px\right] dp. \qquad \text{(ii)}$$

To get the wave function $\psi(x, t)$, multiply each $a(p, 0)$ in (ii) by $\exp\left[-\frac{i}{\hbar}\frac{p^2}{2m} t\right]$. Using the expression for $a(p, 0)$ from (i), this gives,

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \frac{1}{(2\pi)^{1/4}} \sqrt{\frac{a}{\hbar}} \int_{-\infty}^{\infty} \exp\left[-\frac{a^2 (p - p_0)^2}{4\hbar^2}\right] \exp\left[-\frac{i}{\hbar}\frac{p^2}{2m} t\right] \exp\left[\frac{i}{\hbar} px\right] dp.$$

When you evaluate this (with the help of your mathematics friends), you get

$$\psi(x, t) = B \exp\left[\frac{i}{\hbar} p_0 x\right] \exp\left[-\frac{\left(x - \frac{p_0}{m} t\right)^2}{a^2 + \frac{2i\hbar t}{m}}\right] \qquad (9.12)$$

$$= B \exp\left[\frac{i}{\hbar} p_0 x\right] \exp\left[-\frac{\left(x - \frac{p_0}{m} t\right)^2 \left(a^2 - \frac{2i\hbar t}{m}\right)}{a^4 + \frac{4\hbar^2 t^2}{m^2}}\right]$$

$$= B\exp\left[-\frac{a^2\left(x-\frac{p_0}{m}t\right)^2}{a^4+\frac{4\hbar^2t^2}{m^2}}\right]\exp\left[i\left(\frac{p_0}{\hbar}x+\frac{2\left(x-\frac{p_0}{m}t\right)^2\frac{\hbar t}{m}}{a^4+\frac{4\hbar^2t^2}{m^2}}\right)\right]. \qquad (9.13)$$

In this, B is a constant, independent of x. The probability density is

$$|\psi(x,t)|^2 = |B|^2\exp\left[-\frac{\left(x-\frac{p_0}{m}t\right)^2}{\frac{a^2}{2}+\frac{2\hbar^2t^2}{m^2a^2}}\right] \qquad (9.14)$$

$$= |B|^2\exp\left[-\left(x-\frac{p_0}{m}t\right)^2\frac{1}{b^2}\right] \qquad \text{(iii)}$$

where $b=\sqrt{\frac{a^2}{2}+\frac{2\hbar^2t^2}{m^2a^2}}$.

But (iii) is a Gaussian function for any given t. The standard deviation of such a function is

$$\Delta x = \sigma = \frac{b}{\sqrt{2}} = \left(\sqrt{\frac{a^2}{4}+\frac{\hbar^2t^2}{m^2a^2}}\right) \qquad (9.15)$$

which is the position uncertainty at time t. At $t = 0$, $\Delta x = a/2$ as it should be because the wave function is a Gaussian wave function at this time. However, as time passes the spread Δx increases as seen from Equation 9.15. So the wave function spreads as time passes (Figure 9.2).

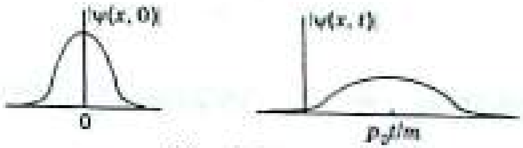


Fig. 9.2

Writing $\frac{a}{2}=\Delta x_0$, the initial spread, the spread at time t is $\Delta x = \sqrt{(\Delta x_0)^2+\frac{\hbar^2t^2}{4m^2(\Delta x_0)^2}}$

You can see that the spread is faster if Δx_0 is small. If you produce a very localized wave function, it will soon spread out. If you think of producing a delta function wave function, in no time it will spread to infinite width.

As a passing remark, $a(p,0)$ is the momentum wave function at time $t=0$ and $|a(p,0)|^2\,dp$ gives the probability of momentum being found in the range p to $p + dp$ at this time. The value of $a(p,0)$ is replaced by

$$a(p,t) = a(p,0)\,e^{-\frac{i}{\hbar}\frac{p^2}{2m}t}$$

to get the expansion at time t. $a(p,t)$ is the momentum wave function at time t and $|a(p,t)|^2\,dp$ gives the probability of momentum being found in the range p to $p + dp$ at this time. As $|a(p,t)|^2=|a(p,0)|^2$, the probability of momentum being found in the range p to $p + dp$ remains constant as time passes. This also means that $\langle p_x\rangle$ and $\left\langle p_x^2\right\rangle$ do not change with time. Thus the momentum uncertainty Δp_x remains constant as the wave function spreads with time. The product $\Delta x\,\Delta p_x$ thus increases.

Is the wave packet $\psi(x,t)$ given by Equation 9.12 not Gaussian at time other than $t = 0$? Look back how I had defined a Gaussian wave packet (Chapter-5). I had stated two conditions. If I write

$$\psi(x) = |\psi(x)| e^{i\phi}$$

$|\psi(x)|$ should be a Gaussian function and ϕ should be proportional to x. With $\psi(x,t)$ given by Equation 9.12, the first condition is satisfied but the second is not.

9.4 Stationary states

Suppose, the wave function of a particle at a given time $t = 0$ is itself an eigenfunction $|\phi_i\rangle$ of the Hamiltonian. Thus,

$$|\psi(0)\rangle = |\phi_i\rangle . \qquad \text{(i)}$$

What would be the wave function at time t? According to our scheme, we should expand $|\psi(0)\rangle$ as a linear combination of the eigenfunctions of the Hamiltonian. But expression (i) itself is such an expansion. There is only one term in the expansion. Using Equation 9.6,

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}E_i t}|\phi_i\rangle$$

or
$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}E_i t}|\psi(0)\rangle \qquad (9.16)$$

This is a very special situation. As time passes, the wave function gets multiplied by a factor $e^{-\frac{i}{\hbar}E_i t}$ which has no dependence on x. So $|\psi(t)\rangle$ and $|\psi(0)\rangle$ have the same functional form (as a function of x) and differ only by a multiplying factor. Hence they represent the same state and so all measurable quantities of the system remain constant as time passes. Such states are therefore called *stationary states*.

Example 9.1

The wave function of a particle at $t = 0$ is an eigenfunction of the Hamiltonian. Show that (a) the probability density of the particle remains constant as time passes (b) the expectation value of any measurable quantity a remains constant as time passes.

Solution: **(a)** The probability density at time t is

$$P(x,t) = |\psi(x,t)|^2 = \left(e^{\frac{i}{\hbar}E_i t}\psi^*(x,0)\right)\left(e^{-\frac{i}{\hbar}E_i t}\psi(x,0)\right) = \psi^*(x,0)\,\psi(x,0) = P(x,0).$$

Thus the probability density remains constant.

(b) Let A be the operator corresponding to the quantity a. The expectation value of a at time t is

$$\begin{aligned}\langle a\rangle(t) &= \langle\psi(t)|A|\psi(t)\rangle \\ &= \int_{-\infty}^{\infty}\psi^*(x,t)\,A\psi(x,t)\,dx \\ &= \int_{-\infty}^{\infty}\left(e^{-\frac{i}{\hbar}E_i t}\psi(x,0)\right)^* A\left(e^{-\frac{i}{\hbar}E_i t}\psi(x,0)\right)dx \\ &= \int_{-\infty}^{\infty}\left(e^{-\frac{i}{\hbar}E_i t}\right)\left(e^{-\frac{i}{\hbar}E_i t}\right)\psi^*(x,0)A\psi(x,0)\,dx\end{aligned}$$

$$= \int_{-\infty}^{\infty} \psi^*(x,0)\, A\psi(x,0)\, dx = \langle a\rangle(0).$$

Thus the expectation value remains constant. I assumed that the operator A operates only on the functions of x and not on time.

Do you see the special importance of energy in quantum mechanics? The operator corresponding to position is called position operator, that corresponding to momentum is called momentum operator and so on. But the operator corresponding to energy is given a special name Hamiltonian (The reasons are of course more historical, it is related to the great physicist Hamilton who contributed immensely in the development of classical mechanics). The eigenfunctions of this operator give the "stationary state" wave functions in which all measurable quantities remain constant as time passes. Also, if you know the eigenvalues and eigenfunctions of the Hamiltonian, you can write the time development of the wave function easily.

9.5 Operators commuting with Hamiltonian

Suppose, a is a dynamical variable for a given system and A is the corresponding Hermitian operator. Also suppose that A commutes with H. For simplicity, assume that all the eigenvalues a_i of A are nondegenerate and the corresponding eigenfunctions are $|\phi_i\rangle$. As A and H commute, the eigenfunctions $|\phi_i\rangle$ are also the eigenfunctions of H, and form a basis for the state space. Thus,

$$A|\phi_i\rangle = a_i|\phi_i\rangle$$

and

$$H|\phi_i\rangle = E_i|\phi_i\rangle.$$

Suppose, the wave function of the particle at time $t = 0$ is given by $|\psi(0)\rangle$. We can expand it in terms of $|\phi_i\rangle$ to get

$$|\psi(0)\rangle = \sum_i c_i(0)|\phi_i\rangle. \quad \text{(i)}$$

The wave function at time t will be

$$|\psi(t)\rangle = \sum_i c_i(0)\, e^{-\frac{i}{\hbar}E_i t}|\phi_i\rangle$$

$$= \sum_i c_i(t)|\phi_i\rangle. \quad \text{(ii)}$$

Suppose the variable a is measured at time t. What is the probability of getting the value a_i? Equation (ii) is the expansion of the wave function (at time t) in terms of the eigenfunctions of A. The eigenfunction corresponding to the eigenvalue a_i is $|\phi_i\rangle$. Thus the probability of getting a_i is equal to the square of the absolute value of the coefficient of $|\phi_i\rangle$.

$$P_i = |c_i(t)|^2 = \left|c_i(0)\, e^{-\frac{i}{\hbar}E_i t}\right|^2 = |c_i(0)|^2.$$

But this is also the probability of getting a_i at $t = 0$ (from Equation (i)). Thus the probability of getting the value a_i in the measurement of a remains constant with respect to time. Accordingly, the expectation value $\langle a\rangle, \langle a^2\rangle$, the uncertainty Δa, all remain constant with respect to time. We therefore say that a is a *constant of motion*.

Note that the state of the particle $|\psi\rangle$ need not be a stationary state. In the previous section I had shown that if the wave function $|\psi\rangle$ is an eigenfunction of the Hamiltonian, all measurable quantities for the particle remain constant in time. Such states are stationary states. In this section I have not assumed that the wave function of the particle is an eigenfunction of the Hamiltonian. Hence not all measurable quantities are guaranteed to be constant. But the quantity a, for which the corresponding operator A commutes with the Hamiltonian, remains constant, i.e., the probability distribution for various values of a remains constant.

Also note that, the wave function $\psi(0)$ need not be an eigen function of A as well. So the value of a need not be definite, even though it is a constant of motion.

9.6 Ernfest Theorem

Suppose the system has a wave function $|\psi(t)\rangle$ at time t and a is a dynamical variable. The expectation value of a, in general, changes with time. We have,

$$\langle a\rangle(t) = \langle\psi(t)|\mathrm{A}|\psi(t)\rangle$$

where A is the operator corresponding to a. Let us calculate the rate at which this value changes with time. We have,

$$\frac{d}{dt}\langle a\rangle = \frac{d}{dt}\langle\psi(t)|\mathrm{A}|\psi(t)\rangle$$

$$= \left\langle\frac{\partial}{\partial t}\psi(t)\,|\,\mathrm{A}\,|\,\psi(t)\right\rangle + \left\langle\psi(t)\,|\,\frac{\partial\mathrm{A}}{\partial t}\,|\,\psi(t)\right\rangle + \left\langle\psi(t)\,|\,\mathrm{A}\,|\,\frac{\partial}{\partial t}\psi(t)\right\rangle . \qquad \text{(i)}$$

The term $\frac{\partial\mathrm{A}}{\partial t}$ is zero if the operator A does not explicitly contain time in its expression. Operators like x, $-i\hbar\frac{d}{dx}$, $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$, etc., do not explicitly contain time. But there are cases where the operator does contain time explicitly. The electric field associated with light is like $\mathbf{E} = \mathbf{E}_0\cos(\omega t - kx)$. When such a field interacts with an atom, the energy operator becomes time dependent. I will continue with conservative systems for which the operators do not explicitly contain time. Let us go back to equation (i). We have,

$$\mathrm{H}|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

or

$$\frac{\partial}{\partial t}|\psi(t)\rangle = \frac{1}{i\hbar}\mathrm{H}|\psi(t)\rangle . \qquad \text{(ii)}$$

From this,

$$\left\langle\frac{\partial}{\partial t}\psi(t)\right| = -\frac{1}{i\hbar}\langle\psi(t)|\mathrm{H} \qquad \text{(iii)}$$

Using (ii) and (iii) in (i),

$$\frac{d}{dt}\langle a\rangle = -\frac{1}{i\hbar}\langle\psi|\mathrm{HA}|\psi\rangle + \frac{1}{i\hbar}\langle\psi|\mathrm{AH}|\psi\rangle$$

$$= \frac{1}{i\hbar}\langle\psi|\mathrm{AH}-\mathrm{HA}|\psi\rangle$$

$$= \frac{1}{i\hbar}\langle[\mathrm{A},\mathrm{H}]\rangle . \qquad (9.17)$$

If A commutes with the Hamiltonian, $[\mathrm{A},\mathrm{H}] = 0$ and $\langle a\rangle$ does not depend on time, a result that I derived in the previous section.

An interesting result is obtained when one calculates $\frac{d}{dt}\langle x\rangle$ and $\frac{d}{dt}\langle p_x\rangle$ for a typical situation of one-dimensional particle dynamics. In elementary classical mechanics you must have studied motion of a particle subjected to a variety of forces such as the force due to gravity, force due to a spring and so on. For conservative systems, you can talk in terms of potential energy instead of force. As you know, quantum physicists use the word potential for what is generally mentioned as potential energy in classical mechanics. Let us consider a particle of mass m subjected to a potential $V(x)$. I am considering only one-dimensional situations. The Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) = \frac{P_x^2}{2m} + V$$

where $P_x = -i\hbar\frac{d}{dx}$ is the operator for linear momentum.

$$\frac{d}{dt}\langle x\rangle = \frac{1}{i\hbar}\langle [X, H]\rangle = \frac{1}{i\hbar}\left\langle\left[X, \frac{P_x^2}{2m} + V\right]\right\rangle = \frac{1}{i\hbar}\left\langle\left[X, \frac{P_x^2}{2m}\right]\right\rangle + \frac{1}{i\hbar}\langle [X, V]\rangle.$$

The second commutator is zero, because both the operators are multiplication type. The first commutator is

$$\left[X, \frac{P_x^2}{2m}\right] = \frac{1}{2m}\left[X, P_x^2\right]$$

$$= \frac{1}{2m}\left[P_x[X, P_x] + [X, P_x]P_x\right]$$

$$= \frac{1}{2m}\left[P_x(i\hbar) + (i\hbar)P_x\right] = \frac{i\hbar}{m}P_x.$$

Thus, $$\frac{d}{dt}\langle x\rangle = \frac{1}{i\hbar}\left\langle\frac{i\hbar}{m}P_x\right\rangle$$

or $$\frac{d}{dt}\langle x\rangle = \frac{\langle p_x\rangle}{m}. \tag{9.18}$$

This relation resembles the classical definition of linear momentum, $p_x = mv_x$ giving $\frac{dx}{dt} = \frac{p_x}{m}$. The expectation values of x and p_x are related by an equation similar to that in classical mechanics.

Let us now check $\frac{d}{dt}\langle p_x\rangle$.

$$\frac{d}{dt}\langle p_x\rangle = \frac{1}{i\hbar}\langle [P_x, H]\rangle$$

$$= \frac{1}{i\hbar}\left\langle\left[P_x, \frac{P_x^2}{2m} + V\right]\right\rangle$$

$$= \frac{1}{i\hbar}\left\langle\left[P_x, \frac{P_x^2}{2m}\right]\right\rangle + \frac{1}{i\hbar}\langle [P_x, V]\rangle. \tag{iv}$$

The first commutator is zero because both the operators are differentiation type. To see the effect of the second commutator, let us operate it on an arbitrary function $f(x)$.

$$[P_x, V(x)]f(x) = P_x V f(x) - V P_x f(x)$$

$$= P_x[Vf(x)] - V[P_x f(x)]$$

$$= -i\hbar\frac{d}{dx}[V(x)f(x)] - V(x)\left[-i\hbar\frac{d}{dx}f(x)\right]$$

$$= \left[-i\hbar\frac{dV(x)}{dx}\right]f(x).$$

(9.19)

Thus $$[P_x, V] = -i\hbar\frac{dV(x)}{dx}$$

and from (iv), (9.20)

$$\frac{d}{dt}\langle p_x\rangle = \left\langle -\frac{dV(x)}{dx}\right\rangle$$

In classical mechanics, we recognize $-\frac{dV(x)}{dx}$ as the force $F(x)$ on the particle. Newton's second law can be written as

$$\frac{dp_x}{dt} = -\frac{dV(x)}{dx}$$

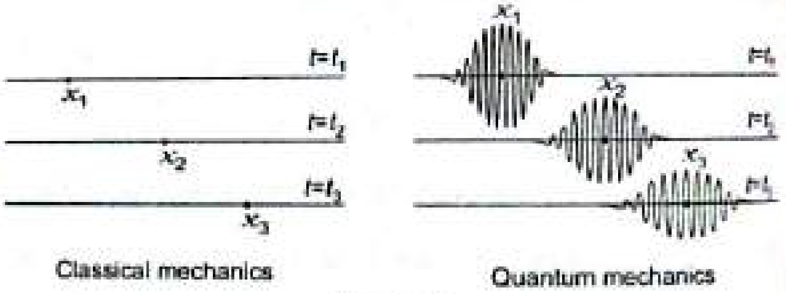
for one-dimensional motion. Equation 9.20 resembles very much with this. Once again the expectation values follow a relation very similar to that in classical mechanics. Equations 9.13 and 9.15 are called Ernfest Theorems.

9.7 Quantum mechanics to classical mechanics

In classical mechanics, a particle is treated as localized in a very small volume, like a point. The force, in general, depends on where the particle is. As time passes, the location of the particle changes and so does the force. At any time, the position x and the force $F(x)$ satisfy the equation of motion

$$m\frac{d^2x}{dt^2} = F(x).$$

In quantum mechanics, the state of the particle at any time is described by a wave packet. The location of the particle is not definite at any given instant. But we talk of the average or expectation value $x_m = \langle x\rangle$ of the particle's position at a given time. For example, $\langle x\rangle$ for a Gaussian wave packet will be right at the middle of the wave packet, about which $|\psi(x,t)|^2$ is symmetric at that time. If you look at this point in the wave packet, it moves as a function of time, and the relation is



Classical mechanics   Quantum mechanics

Fig. 9.3

$$\frac{d^2x_m}{dt^2} = \frac{d}{dt}\left[\frac{dx_m}{dt}\right]$$

$$= \frac{d}{dt}\left[\frac{d\langle x\rangle}{dt}\right] = \frac{d}{dt}\left[\frac{\langle p_x\rangle}{m}\right] = \frac{1}{m}\left\langle -\frac{dV}{dx}\right\rangle$$

or, $$\frac{d^2x_m}{dt^2} = \frac{f(x)}{m}$$ (9.21)

where $$f(x) = \left\langle -\frac{dV}{dx}\right\rangle.$$

Does this $f(x)$ represent the force at $x = x_m$? In general, no. If this had been the case, Equation 9.16 would exactly represent Newton's second law for the expectation value x_m. But $\left\langle -\frac{dV}{dx} \right\rangle$ is the average calculated over entire region of space where the wave packet has appreciable value. This, in general, is not equal to the value of $-\frac{dV}{dx}$ at the point $x = x_m$.

However, the two quantities are not very different if the wave function is highly localized. If the spread in the wave packet is small, say from $x_m - \Delta$ to $x_m + \Delta$, for any function $g(x)$,

$$\begin{aligned}
\langle g(x) \rangle &= \int_{x_m - \Delta}^{x_m + \Delta} g(x) |\psi(x)|^2 \, dx \\
&\approx \int_{x_m - \Delta}^{x_m + \Delta} g(x_m) |\psi(x)|^2 \, dx \\
&= g(x_m) \int_{x_m - \Delta}^{x_m + \Delta} |\psi(x)|^2 \, dx \\
&= g(x_m).
\end{aligned}$$

Using this result, Equation 9.16 can be written as

$$\frac{d^2 x_m}{dt^2} = \frac{f(x_m)}{m}. \tag{9.22}$$

Thus in such a case, the time dependence of the average value of x obtained from the Schrödinger equation becomes identical to what you would write using Newton's laws of motion.

9.8 You learned in this chapter

- If no measurement is made on a particle, its wave function evolves in time according to the Schrödinger equation
$$\mathrm{H}|\psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle.$$
- If the wave function at $t = 0$ is written as a linear combination of energy eigenfunctions, $\psi(x, 0) = \sum_i c_i |\phi_i\rangle$, that at time t will be $\psi(x, t) = \sum_i c_i \, e^{-\frac{i}{\hbar} E_i t} |\phi_i\rangle$ where E_i is the eigenvalue corresponding to the eigenfunction $|\phi_i\rangle$.
- A Gaussian wave packet corresponding to a free particle spreads as time passes. The probability density function $|\psi(x, t)|^2$ remains a Gaussian function but the uncertainty product $\Delta x \, \Delta p_x$ gradually increases with time.
- If the wave function at any given time is an eigenfunction of the Hamiltonian, all measurable properties of the system remain constant as time passes. Such states are called stationary states.
- If the operator corresponding to a measurable quantity commutes with the Hamiltonian, that quantity is a constant of motion.
- For a dynamical variable a with the corresponding operator A,
$$\frac{d}{dt} \langle a \rangle = \frac{1}{i\hbar} [\mathrm{A}, \mathrm{H}].$$

- The average values of the position x, momentum p and dV/dx of a particle subjected to potential $V(x)$, are related as

$$\frac{d}{dt}\langle x\rangle = \frac{\langle p_x\rangle}{m} \text{ and } \frac{d}{dt}\langle p_x\rangle = \left\langle -\frac{dV}{dx}\right\rangle.$$

- For particles represented by highly localized wave packets, the above equations reduce to Newton's equations of motion.

Solved Problems

1. The stationary states of a system are given by $|\phi_i\rangle$ and the corresponding energies by E_i. At time $t = 0$, the wave function is $|\psi(0)\rangle = \frac{1}{\sqrt{6}}|\phi_1\rangle + \frac{1}{\sqrt{3}}|\phi_2\rangle + \sqrt{\frac{1}{2}}|\phi_3\rangle$. What is the wave function at time t?

Solution: The wave function at time t is,

$$|\psi(t)\rangle = \frac{1}{\sqrt{6}}e^{-\frac{i}{\hbar}E_1 t}|\phi_1\rangle + \frac{1}{\sqrt{3}}e^{-\frac{i}{\hbar}E_2 t}|\phi_2\rangle + \sqrt{\frac{1}{2}}e^{-\frac{i}{\hbar}E_3 t}|\phi_3\rangle.$$

2. The wave function of an electron moving along the x-axis with a kinetic energy 100 eV is in the form of a wave packet with a spread of 1.0 nm at a certain place. Estimate the spread of the wave packet as it moves through 10 cm.

Solution: To estimate the spread, assume that the wave packet is Gaussian. The spread of a Gaussian wave packet at time t is given by

$$\Delta x = \sqrt{\frac{a^2}{4} + \frac{\hbar^2 t^2}{m^2 a^2}}$$

where $a/2 = \Delta x_0$ is the spread of the wave packet at $t = 0$. In the present case, the kinetic energy 100 eV is much smaller than the rest mass energy 511 keV of the electron. So the speed is nonrelativistic and you can write $t = \frac{x}{v}$ for the classical description where x is the displacement in time t.

$$\Delta x = \sqrt{(\Delta x_0)^2 + \frac{\hbar^2 x^2}{4m^2(\Delta x_0)^2 v^2}}$$

$$= \sqrt{(\Delta x_0)^2 + \frac{\hbar^2 x^2}{8m(\Delta x_0)^2 K}}$$

where K is the kinetic energy. For electron, $\frac{\hbar^2}{2m} = 0.038 \text{ eV.nm}^2$. Thus,

$$(\Delta x)^2 = (1.0\text{ nm})^2 + \frac{0.038\text{ eV.nm}^2 \times (10\text{ cm})^2}{4 \times (1.0\text{ nm})^2 \times (100\text{ eV})}$$

$$= (1.0\text{ nm})^2 + \frac{0.038\text{eV.nm}^2 \times \left(10^8\text{nm}\right)^2}{4 \times (1.0\text{nm})^2 \times (100\text{eV})}$$

$$= (1.0\text{ nm})^2 + 95 \times 10^{10}\text{nm}^2$$

Thus $\Delta x \approx 10^{6}\,\text{nm}$.

The width increases by a factor of about 10^{6}.

3. Prove that $\frac{d}{dt}\int_{-\infty}^{\infty}\psi^{*}(x,t)\,\psi(x,t)\,dx = 0$

Solution: The given expression is

$$\frac{d}{dt}\langle\psi|\psi\rangle = \left\langle\frac{\partial\psi}{\partial t}\middle|\psi\right\rangle + \left\langle\psi\middle|\frac{\partial\psi}{\partial t}\right\rangle. \tag{i}$$

From the Schrödinger equation,

$$\frac{\partial|\psi\rangle}{\partial t} = \frac{1}{i\hbar}\mathrm{H}|\psi\rangle.$$

Using in (i),

$$\frac{d}{dt}\langle\psi|\psi\rangle = \left\langle\frac{1}{i\hbar}\mathrm{H}\psi\middle|\psi\right\rangle + \left\langle\psi\middle|\frac{1}{i\hbar}\mathrm{H}\psi\right\rangle$$

$$= -\frac{1}{i\hbar}\langle\psi|\mathrm{H}|\psi\rangle + \frac{1}{i\hbar}\langle\psi|\mathrm{H}|\psi\rangle = 0.$$

Note how I wrote $-\frac{1}{i\hbar}$ in the first term. As $\frac{1}{i\hbar}$ appearing in bra was taken out, it became $-\frac{1}{i\hbar}$.

You could have easily guessed the result proved above. The integral given in the question is the probability of finding the particle somewhere in the whole space and this must be 1. Thus it remains constant in time and hence the time derivative is zero.

4. Prove that $\frac{d}{dt}\langle\psi_1|\mathrm{X}|\psi_2\rangle = \frac{1}{m}\langle\psi_1|\mathrm{P_x}|\psi_2\rangle$.

Solution:

$$\frac{d}{dt}\langle\psi_1|\mathrm{X}|\psi_2\rangle = \left\langle\frac{\partial\psi_1}{\partial t}\middle|\mathrm{X}\middle|\psi_2\right\rangle + \left\langle\psi_1\middle|\mathrm{X}\middle|\frac{\partial\psi_2}{\partial t}\right\rangle$$

$$= \left\langle\frac{1}{i\hbar}\mathrm{H}\psi_1\middle|\mathrm{X}\middle|\psi_2\right\rangle + \left\langle\psi_1\middle|\mathrm{X}\middle|\frac{1}{i\hbar}\mathrm{H}\psi_2\right\rangle$$

$$= -\frac{1}{i\hbar}\langle\psi_1|\mathrm{HX}|\psi_2\rangle + \frac{1}{i\hbar}\langle\psi_1|\mathrm{XH}|\psi_2\rangle$$

$$= \frac{1}{i\hbar}\langle\psi_1|\mathrm{XH}-\mathrm{HX}|\psi_2\rangle = \frac{1}{i\hbar}\langle\psi_1|[\mathrm{X},\mathrm{H}]|\psi_2\rangle.$$

But

$$[\mathrm{X},\mathrm{H}] = \left[\mathrm{X}, \frac{\mathrm{P_x^2}}{2m} + \mathrm{V}(x)\right] = \left[\mathrm{X}, \frac{\mathrm{P_x^2}}{2m}\right] = \frac{i\hbar}{m}\mathrm{P_x}.$$

So,

$$\frac{d}{dt}\langle\psi_1|\mathrm{X}|\psi_2\rangle = \frac{1}{m}\langle\psi_1|\mathrm{P_x}|\psi_2\rangle.$$

5. Prove that $\frac{d}{dt}\langle x^2\rangle = \frac{1}{m}\langle\mathrm{XP_x} + \mathrm{P_xX}\rangle$.

Solution:

$$\frac{d}{dt}\langle x^2\rangle = \frac{1}{i\hbar}\left\langle\left[\mathrm{X}^2,\mathrm{H}\right]\right\rangle$$

$$= \frac{1}{i\hbar}\left\langle\left[\mathrm{X}^2, \frac{\mathrm{P_x^2}}{2m} + \mathrm{V}(x)\right]\right\rangle$$

$$= \frac{1}{2mi\hbar}\left\langle \left[X^2, P_x^2\right] \right\rangle$$

$$= \frac{1}{2mi\hbar}\left\langle P_x\left[X^2, P_x\right] + \left[X^2, P_x\right]P_x \right\rangle$$

$$= \frac{1}{2mi\hbar}\left\langle P_x(2i\hbar X) + (2i\hbar X)P_x \right\rangle$$

$$= \frac{1}{m}\langle P_xX + XP_x\rangle = \frac{1}{m}\langle XP_x + P_xX\rangle .$$

6. A particle moves in a linear potential $V(x) = -kx$, (i.e. under a constant force condition). Show that $\langle x\rangle$ follows rigorously the same time evolution as given by Newton's laws.

Solution. The equation for $\langle x\rangle$ is

$$\frac{d^2}{dt^2}\langle x\rangle = \frac{1}{m}\left\langle -\frac{dV}{dx}\right\rangle . \qquad \text{(i)}$$

As $V(x) = -kx$, $-\frac{dV}{dx} = k$ which is independent of x and equals the force in classical physics. The expectation value $\left\langle -\frac{dV}{dx}\right\rangle$ is also equal to k because $-dV/dx$ is independent of x. Thus (i) becomes

$$\frac{d^2}{dt^2}\langle x\rangle = \frac{k}{m} = \frac{F}{m} .$$

According to the Newton's law, the position x of the particle moves in accordance with the equation $\frac{d^2x}{dt^2} = \frac{F}{m}$. So, $\langle x\rangle$ evolves in time rigorously the same way as x evolves in classical physics.

7. Let $P_x = P_{1x} + P_{2x}$ be the operator for the total linear momentum of an isolated system of two particles labeled 1 and 2. The potential energy depends only on the relative separation between the particles. Show that $\langle P_x\rangle$ remains constant in time.

Solution: As the potential energy depends only on the separation between the particles, it may be written as $V(x_1 - x_2)$. Let me write $x_1 - x_2 = x_{12}$. The Hamiltonian is

$$H = \frac{1}{2m}\left(P_{1x}^2 + P_{2x}^2\right) + V(x_{12}) .$$

We have

$$\frac{d\langle P_x\rangle}{dt} = \frac{1}{i\hbar}[P_x, H]$$

$$= \frac{1}{i\hbar}[P_{1x} + P_{2x}, H]$$

$$= \frac{1}{2mi\hbar}\left[P_{1x} + P_{2x}, P_{1x}^2 + P_{2x}^2\right] + \frac{1}{i\hbar}[P_{1x} + P_{2x}, V(x_{12})]$$

$$= \frac{1}{i\hbar}[P_{1x} + P_{2x}, V(x_{12})]$$

or,

$$\frac{d\langle P_x\rangle}{dt} = \frac{1}{i\hbar}[(P_{1x} + P_{2x})V(x_{12}) - V(x_{12})(P_{1x} + P_{2x})] . \qquad \text{(i)}$$

Let us see the effect of each of the two terms in the square bracket on an arbitrary function $f(x_1, x_2)$. The first term operating on $f(x_1, x_2)$ gives

$$\begin{aligned}
&\left[(P_{1x}+P_{2x})V(x_{12})\right]f(x_1,x_2)\\
&=(P_{1x}+P_{2x})[V(x_{12})f(x_1,x_2)]\\
&=-i\hbar\left[\frac{d}{dx_1}+\frac{d}{dx_2}\right][V(x_{12})f(x_1,x_2)]\\
&=-i\hbar\left[\frac{d}{dx_1}[V(x_{12})f(x_1,x_2)]+\frac{d}{dx_2}[V(x_{12})f(x_1,x_2)]\right]\\
&=-i\hbar\left[V(x_{12})\frac{df(x_1,x_2)}{dx_1}+f(x_1,x_2)\frac{dV(x_{12})}{dx_1}+V(x_{12})\frac{df(x_1,x_2)}{dx_2}+f(x_1,x_2)\frac{dV(x_{12})}{dx_2}\right]. \qquad \text{(ii)}
\end{aligned}$$

Now $$\frac{dV(x_{12})}{dx_1}=\frac{dV(x_1-x_2)}{dx_1}=\frac{dV(x_1-x_2)}{d(x_1-x_2)}\cdot\frac{d(x_1-x_2)}{dx_1}=\frac{dV(x_1-x_2)}{d(x_1-x_2)}$$

and $$\frac{dV(x_{12})}{dx_2}=\frac{dV(x_1-x_2)}{dx_2}=\frac{dV(x_1-x_2)}{d(x_1-x_2)}\cdot\frac{d(x_1-x_2)}{dx_2}=-\frac{dV(x_1-x_2)}{d(x_1-x_2)}.$$

So the second and fourth terms in the square bracket in (ii) cancel. Thus

$$\left[(P_{1x}+P_{2x})V(x_{12})\right]f(x_1,x_2)=-i\hbar V(x_{12})\left[\frac{df(x_1,x_2)}{dx_1}+\frac{df(x_1,x_2)}{dx_2}\right]. \qquad \text{(iii)}$$

The second term in the square bracket in (i) operating on $f(x_1,x_2)$ gives

$$\begin{aligned}
&\left[V(x_{12})(P_{1x}+P_{2x})\right]f(x_1,x_2)\\
&=V(x_{12})(-i\hbar)\left[\frac{d}{dx_1}+\frac{d}{dx_2}\right]f(x_1,x_2)\\
&=-i\hbar V(x_{12})\left[\frac{df(x_1,x_2)}{dx_1}+\frac{df(x_1,x_2)}{dx_2}\right]
\end{aligned}$$

which is the same as (iii). Thus

$$V(x_{12})(P_{1x}+P_{2x})-(P_{1x}+P_{2x})V(x_{12})=0\,.$$

Thus, from (i), $\dfrac{d\langle P_x\rangle}{dt}=0$ and hence $\langle P_x\rangle=\text{constant}$.

This result is analogous to the principle of conservation of linear momentum in classical mechanics, which states that the linear momentum of an isolated system remains constant in time.

EXERCISES

1. Let $|\psi_1\rangle=\frac{1}{\sqrt{2}}|\phi_1\rangle+\frac{1}{\sqrt{2}}|\phi_2\rangle$ and $|\psi_2\rangle=\frac{1}{\sqrt{3}}|\phi_1\rangle+\sqrt{\frac{2}{3}}|\phi_2\rangle$ be two possible wave functions of a particle at $t=0$. Here $|\phi_1\rangle$ and $|\phi_2\rangle$ are normalized eigenfunctions of the Hamiltonian with different eigenvalues E_1 and E_2.

   (a) Convince yourself that $|\psi_1\rangle$ and $|\psi_2\rangle$ are normalized.

   (b) Write $|\psi_1(t)\rangle$ and $|\psi_2(t)\rangle$ at time t.

   (c) Explicitly calculate $\langle\psi_1(t)|\psi_2(t)\rangle$ and show that it is equal to $\langle\psi_1(0)|\psi_2(0)\rangle$.

2 The eigenstates of the Hamiltonian of a quantum system are $|\phi_1\rangle, |\phi_2\rangle$ and $|\phi_3\rangle$. The corresponding energies are $E_0, 2E_0$ and $3E_0$. At time $t = 0$, the state vector $|\psi\rangle$ has the following scalar products, $\langle\phi_1|\psi\rangle = 3/5$, $\langle\phi_2|\psi\rangle = \frac{2\sqrt{2}}{5}$, $\langle\phi_3|\psi\rangle = \frac{2\sqrt{2}}{5}$. Find these scalar products at time $t = \frac{\pi\hbar}{E_0}$. **Ans.** $-\frac{3}{5}, \frac{2\sqrt{2}}{5}, -\frac{2\sqrt{2}}{5}$

3. According to the classical description, an electron moves with kinetic energy 1 keV. It corresponds to a Gaussian wave packet of width 10 nm. Find the time in which the width increases to 20 nm.

Ans. 3×10^{-12}s

4. We have derived $[P_x, V] = \left[-i\hbar\frac{d}{dx}V(x)\right]$. Can you write the RHS as P_xV? The LHS is $P_xV - VP_x$. Are we suggesting that VP_x is zero?

5. Let $\psi_1(x,t)$ and $\psi_2(x,t)$ be two wave functions, each satisfying the Schrödinger equation $H\psi = i\hbar\frac{\partial}{\partial t}\psi$ for the same Hamiltonian. Show that the scalar product of the two wave functions is constant in time.

6. The Hamiltonian of a particle is $H = \frac{P_x^2}{2m} + V(x)$. Prove that $\frac{d^2}{dt^2}\langle\psi_1|X|\psi_2\rangle = -\frac{1}{m}\langle\psi_1|\frac{dV(x)}{dx}|\psi_2\rangle$ for any two wave functions $|\psi_1\rangle$ and $|\psi_2\rangle$.

7. The wave function of a free particle at time $t = 0$ is $\psi(0) = e^{-|x|/a}e^{\frac{i}{\hbar}p_0x}$. The uncertainty Δp_x of the momentum in this state is $\hbar/a$. Without doing any explicit integration find the uncertainty of the momentum at a later time t. **Ans.** $\hbar/a$

8. Show that $\frac{d}{dt}\langle K\rangle = -\frac{1}{2m}\left\langle P_x\frac{dV(x)}{dx} + \frac{dV(x)}{dx}P_x\right\rangle$ where K is the kinetic energy and $V(x)$ is the potential energy operator.

9. A particle moves under a parabolic potential $V(x) = \frac{1}{2}kx^2$. Show that $\langle x\rangle$ evolves in time in a manner identical to that given by classical physics.

10. A particle is subjected to a potential $V(x) = \lambda X^n$. Show that $2\langle K\rangle = n\langle V\rangle$ in a stationary state where K and V are kinetic energy and potential energy operators.

10

Can Energy be Created or Destroyed — Energy–Time Uncertainty

10.1 Energy–time uncertainty principle

If the wave function of a system is an eigenfunction of the Hamiltonian, its energy is definite. The uncertainty in energy ΔE is therefore zero. At the same time, the state of the system is a stationary state and no property changes with time. The system remains in this state for infinite time. Let me call this time Δt. So $\Delta t = \infty$. If the wave function is not an eigenfunction of the Hamiltonian, the energy is not definite so that there is a finite uncertainty ΔE in it. Also the state evolves with time according to the Schrödinger equation and changes "appreciably" in a finite time Δt. I will show that $(\Delta E)(\Delta t)$ is of the order of $\hbar$, that is,

$$(\Delta E)(\Delta t) \approx \hbar . \tag{10.1}$$

This principle is called the *Heisenberg's energy–time uncertainty principle*. Interpretation of Δt is not the same as that of ΔE. It is not the uncertainty in time in the sense I had introduced uncertainty in position or momentum. It is the time taken by the system to evolve considerably. Let me explain this more explicitly.

10.2 Time evolution of a simple wave function

Suppose $|\phi_1\rangle$ and $|\phi_2\rangle$ are two eigenfunctions of the Hamiltonian of a system with eigenvalues E_1 and E_2. Let the wave function of the system at time $t = 0$ be

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}\left(|\phi_1\rangle + |\phi_2\rangle\right).$$

The wave function at time t is

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(|\phi_1\rangle e^{-\frac{i}{\hbar}E_1 t} + |\phi_2\rangle e^{-\frac{i}{\hbar}E_2 t}\right).$$

Consider a variable a for which the operator is A. Suppose, it has a non degenerate eigenvalue a_1 and the corresponding eigenfunction is $|\xi_1\rangle$. What is probability that a measurement made at time t gives the value a_1? It is

$$P(t) = \left|\langle \xi_1 | \psi(t)\rangle\right|^2 = \frac{1}{2}\left|\langle \xi_1 | \phi_1\rangle e^{-\frac{i}{\hbar}E_1 t} + \langle \xi_1 | \phi_2\rangle e^{-\frac{i}{\hbar}E_2 t}\right|^2 = \frac{1}{2}\left|c_1 e^{-\frac{i}{\hbar}E_1 t} + c_2 e^{-\frac{i}{\hbar}E_2 t}\right|^2$$

where $c_1 = \langle \xi_1 | \phi_1\rangle$ and $c_2 = \langle \xi_1 | \phi_2\rangle$.

Thus
$$P(t) = \frac{1}{2}\left(c_1 e^{-\frac{i}{\hbar}E_1 t} + c_2 e^{-\frac{i}{\hbar}E_2 t}\right)\left(c_1^* e^{\frac{i}{\hbar}E_1 t} + c_2^* e^{\frac{i}{\hbar}E_2 t}\right)$$

$$= \frac{1}{2}\left(c_1 c_1^* + c_2 c_2^* + c_1 c_2^* e^{\frac{i}{\hbar}(E_2 - E_1)t} + c_1^* c_2 e^{-\frac{i}{\hbar}(E_2 - E_1)t}\right)$$

$$=\frac{1}{2}\left[|c_1|^2+|c_2|^2+\left(c_1c_2^*+c_1^*c_2\right)\cos\left(\frac{E_2-E_1}{\hbar}t\right)+i\left(c_1c_2^*-c_1^*c_2\right)\sin\left(\frac{E_2-E_1}{\hbar}\right)\right].$$

Write $c_1c_2^*+c_1^*c_2=B\sin\varepsilon$ and $i(c_1c_2^*-c_1^*c_2)=B\cos\varepsilon$. Check that

$$B=2|c_1||c_2|\text{and }\varepsilon=\tan^{-1}\frac{c_1c_2^*+c_1^*c_2}{i(c_1c_2^*-c_1^*c_2)}.$$

With these definitions you can write the probability $P(t)$ as

$$P(t)=\frac{1}{2}\left[|c_1|^2+|c_2|^2+2|c_1||c_2|\sin(\omega t+\varepsilon)\right]$$

where $\omega=|(E_2-E_1)|/\hbar$.

The probability changes periodically with time between the maximum value $\frac{1}{2}(|c_1|+|c_2|)^2$ and the minimum value $\frac{1}{2}(|c_1|-|c_2|)^2$. How much time does it take for the probability to 'appreciably' change? The time period of oscillation of $P(t)$ is

$$T=\frac{2\pi}{\omega}=\frac{2\pi\hbar}{|(E_2-E_1)|}.$$

In a time interval small compared to T, there will be no appreciable change. In a time interval $T/4$, it changes from its mean value to an extreme value. The time interval Δt in which the probability of getting a_1 changes appreciably is therefore 'of the order of' $T/4$. I am not very keen about the factor of $1/4$, one can take it as $1/2$ and say that $\Delta t\approx T/2$, or one can take $\Delta t\approx T/10$, etc. That is why I said 'of the order of'.

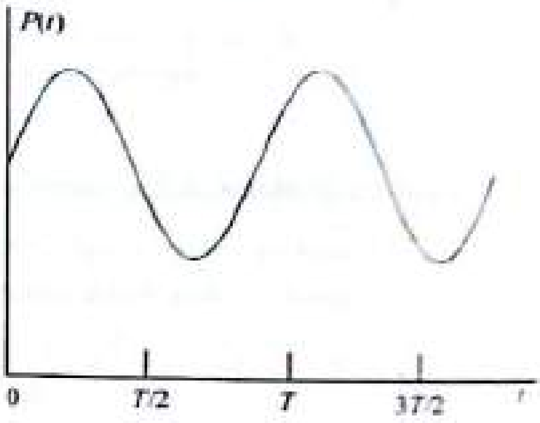


Fig. 10.1

The probability of getting a_1 was an example. It changed because the wave function has changed as time passed. Thus the system has changed its state appreciably in a time,

$$\Delta t\approx\frac{T}{4}=\frac{2\pi\hbar}{4|(E_2-E_1)|}. \tag{i}$$

There are two possible values of energy, E_1 and E_2 in the assumed state $|\psi(0)\rangle$. It remains so even at time t when the wave function has changed to $|\psi(t)\rangle$. At time t, the probability of getting the value E_1 as well as E_2 is 50%. So what is the uncertainty in energy? It is 'of the order of'

$$\Delta E=|E_2-E_1|. \tag{ii}$$

From (i) and (ii),

$$\Delta E\,\Delta t\approx\hbar. \tag{iii}$$

Once again I remind you that I have not used mathematical definition of ΔE or of time Δt. Therefore, the whole discussion is, to some extent, qualitative. That is why I was not keen to do correct arithmetic in getting (iii) from (i) and (ii).

10.3 Natural linewidth of spectral lines

Your physics teacher in STD XII must have taught you Bohr's model of hydrogen atom. There are some particular energies E_0, E_1, E_2,... that a hydrogen atom can have. The state with lowest energy E_0 is called the ground state and the other states are called excited states. These energies are obtained by assuming that the electron revolves around the proton in a hydrogen atom in 'circular orbits' in which the angular momentum mvr is an integral multiple of $\hbar$. The ground state energy comes out to be $E_0 = -13.6$ eV, that in the first excited state is –3.4 eV and so on.

The model described above does not have proper sanction from quantum mechanics. The idea of a definite trajectory is not acceptable because it means you know the position and momentum accurately at the same time. I shall devote a full chapter on the quantum mechanical treatment of hydrogen atom. But the fact remains that if we do a proper quantum mechanics and assume just the Coulomb potential, the energy eigenvalues come out to be the same as those in Bohr's model. So the idea of transition between different states remains valid.

If a hydrogen atom is in an excited state, it makes transition to lower energy states. The average time for which a hydrogen atom stays in an excited state is called the *lifetime* of that state. The lifetime τ for atomic excited states is often of the order of $10^{-8}\,\text{s}$. If you leave a hydrogen atom in the first excited state at $t = 0$ and examine it at $t = 10^{-8}\,\text{s}$, there is a considerable probability that it will be in the ground state. This means, the state of the atom has considerably evolved in a time of about 10^{-8} s. Thus $\Delta t \approx \tau \approx 10^{-8}\,\text{s}$.

Is there an uncertainty ΔE in energy when the atom is in the first excited state? There has to be because if the energy is definite, it will be a stationary state and no measurable property of the system will ever change. Here the properties do change appreciably in a time τ. So the excited state must have an uncertainty $\Delta E \approx \frac{\hbar}{\tau}$ according to the energy–time uncertainty principle.

The ground state is stable. Once in the ground state, the system remains there for any length of time. So there is no uncertainty in energy ($\tau = \infty$, $\hbar/\tau = 0$). I show the energy level diagram schematically in Figure 10.2.

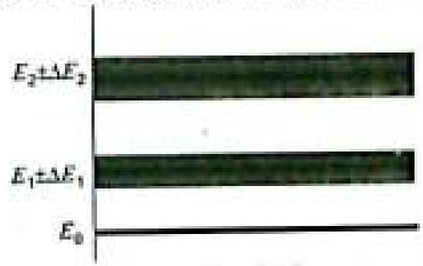


Fig. 10.2

Example 10.1

Estimate the uncertainty ΔE *for the first excited state of a hydrogen atom (life time* $= 10^{-8}\,\text{s}$*).*

Solution: $\Delta E \approx \frac{\hbar}{\tau} \approx \frac{10^{-15}\,\text{eV s}}{10^{-8}\,\text{s}} = 10^{-7}\,\text{eV}$.

Consider a sample of hydrogen gas with lots of atoms in the first exited state. The energy in the ground state is E_0 and that in the first excited state is distributed in the range $E_1 \pm \Delta E$. Here ΔE is the spread in the energy due to energy–time uncertainty. The energy of the emitted photons is therefore distributed in range $(E_1 - E_0) - \Delta E$ to $(E_1 - E_0) + \Delta E$. Correspondingly, the wavelength of the emitted photons is distributed in the range $\lambda - \Delta\lambda$ to $\lambda + \Delta\lambda$. The value of $\Delta\lambda$ can be calculated as follows. Suppose the wavelength of the emitted photon is λ when the first excited state energy is E. Then,

$$\lambda = \frac{hc}{E - E_0}$$

or,
$$\ln \lambda = \ln(hc) - \ln(E - E_0)$$

or,
$$\left|\frac{d\lambda}{\lambda}\right| = \left|\frac{\Delta E}{E - E_0}\right| \approx \frac{10^{-7}\,\text{eV}}{10\,\text{eV}} \approx 10^{-8}.$$

The transition from the first excited state to the ground state in hydrogen atoms gives a mean wavelength of 122 nm. So the actual wavelength will be distributed in the range $122\,(1 \pm 10^{-8})$ nm. The intensity will be maximum at the mean wavelength and it will fall on both sides of this wavelength. The spread in the wavelength of the radiation emitted, during a particular type of transition, due to spread in the energy levels is called *natural linewidth*.

If you determine experimentally the spread in the wavelength in a particular line emitted from hydrogen gas, say in a discharge tube, you will find that this spread is much larger than the natural linewidth. One reason of the increased linewidth is the Doppler broadening as explained below.

The atoms in a gas move in random directions with random speeds. The mean speed is given as

$$v = \sqrt{\frac{8kT}{\pi m}}$$

which comes out to be few hundred meters per second in laboratory conditions. Though this speed is large compared to the speeds encountered in everyday events, it is still small enough So that one can use non relativistic approximation. The radiation, that we receive from the gas, is emitted by these moving atoms and hence the wavelength changes according to the Doppler effect equation,

$$\lambda \approx \lambda_0\left(1 - \frac{v_x}{c}\right)$$

where v_x is the component of the velocity in the direction in which the radiation is received. This component v_x is also distributed randomly, becoming both positive and negative, and this contributes to Doppler broadening.

The above description is valid for all kinds of system emitting spectral lines. Atoms, molecules or nuclei, whenever there is radiation emitted, there will be a natural linewidth given by the Heisenberg energy–time uncertainty principle together with other types of broadening.

10.4 Principle of energy conservation

The total energy of a system remains constant as time passes, provided no external work is done on the system. This is the principle of conservation of energy that I teach in schools. Writing in the equation form

$$E\,(\text{initial}) = E\,(\text{final}) \tag{10.2}$$

where 'initial' and 'final' denote two instants of time.

But now that I have told you so much about quantum mechanics, there is a difficulty in interpreting Equation 10.2. Suppose the state of the system at the 'initial' time is not a stationary state and there is an uncertainty ΔE_1 in the energy. So, the energy may be anything in a range given roughly by $E_1 \pm \Delta E_1$. Similar may be the case at the 'final' instant where the energy may be anything in the range $E_2 \pm \Delta E_2$. So which value do I write for the energy at the 'initial' instant and which for the 'final' instant in (i)? It appears that the law can be applied only approximately as the energies in the two states are themselves uncertain. So there may be an apparent violation of energy conservation. However this uncertainty or apparent violation cannot last for long. An apparent violation of energy ΔE can last for a time $\Delta t \approx \hbar/\Delta E$ only. Thus it may appear to you in certain cases that energy has been created for some time from nowhere and it is lost to unknown sources. But it has to be temporary and the time duration depends on the amount of energy seems to be created and destroyed

This fundamental uncertainty in the interpretation of principle of conservation of energy helps us in a big way to survive as a living body as I discuss in the next section.

10.5 Nuclear fusion

You are here to read this book and I am here to write this book because hydrogen nuclei in the core of the sun are fusing to helium nuclei. Nuclear fusion in the core of the sun releases energy which the sun radiates and that is the lifeline of the earth. The temperature in the core of the sun is about $1.5\times10^7\,\mathrm{K}$. At this temperature, the electrons are all detached from hydrogen atoms leaving behind bare protons. These protons move randomly with an average kinetic energy of $\frac{3}{2}kT = 1.9\ \mathrm{keV}$. The speed corresponding to this kinetic energy comes out to be around $6\times10^5\,\mathrm{m/s}$. Occasionally, two protons moving towards each other come so close that the attractive nuclear force starts dominating over the repulsive Coulomb force. One of the protons then converts itself into a neutron and the other proton combines with this neutron to form a deuteron. A positron and a neutrino are also formed in the process. Such a deuteron then combines with a proton to form the ${}^3_2\mathrm{He}$ nucleus and two such nuclei combine to form a helium nucleus expelling two protons. The positrons combine with electrons to convert themselves completely in gamma photons. The whole cycle may be represented by the following equations.

$$2\times\left[{}^1\mathrm{H}+{}^1\mathrm{H}\rightarrow{}^2\mathrm{H}+e^+ +\nu\right]$$

$$2\times\left[{}^2\mathrm{H}+{}^1\mathrm{H}\rightarrow{}^3\mathrm{He}\right]$$

$${}^3\mathrm{He}+{}^3\mathrm{He}\rightarrow{}^4\mathrm{He}+{}^1\mathrm{H}+{}^1\mathrm{H}$$

$$2\times\left[e^+ + e^- \rightarrow \gamma\right].$$

All this is equivalent to

$$4\,{}^1\mathrm{H}+2e^- \rightarrow {}^4\mathrm{He}+2\nu .$$

At each step the energy is released and the total energy released in the cycle is 26.7 MeV. Let us look at the first step of the series, two protons making a deuteron, in somewhat more detail. The attractive nuclear force between two protons is short ranged. It is effective only when the separation between the protons is not more than few femtometers ($1\ \text{femtometer} = 10^{-15}\,\mathrm{m}$). The average kinetic energy of the protons in the core of the sun is about 1.9 keV. How close can two protons moving towards each other with this kinetic energy come? Let me work it out for you.

Example 10.2

Calculate the closest distance two protons can approach if each has a kinetic energy of 1.9 keV *and moves towards the other.*

Solution: Let us use only the Coulomb force and classical Physics. As the protons move closer to each other, they slow down because of mutual repulsion. At the closet separation the protons will come to rest. Whole of their kinetic energy will convert to potential energy at this stage. So,

$$\frac{e^2}{4\pi\varepsilon_0 r} = 2\times1.9\ \mathrm{keV}$$

or $$\frac{1.44\ \mathrm{eV\,nm}}{r} = 3800\ \mathrm{eV}$$

or $$r = \frac{1.44}{3800}\,\mathrm{nm} \approx 360\ \mathrm{fm}.$$

If the protons return from this separation, there seems no chance of nuclear fusion. This is still about hundred times larger than what is needed for the nuclear force to come into play. This also justifies our assumption made during the calculations that only Coulomb force acts between the protons.

Example 10.3

With what kinetic energy should two protons head towards each other so that their separation can decrease to 4 fm? Use Coulomb's law. What should be the temperature at the core of the sun so that the protons may have this much of average kinetic energy?

Solution: If each proton has a kinetic energy of K, we have

$$2K = \frac{e^2}{4\pi\varepsilon_0(4\ \text{fm})}$$

or $$K = \frac{1}{2} \times \frac{1.44\ \text{eV nm}}{4 \times 10^{-6}\ \text{nm}} = 180\ \text{keV}.$$

The average kinetic energy and the temperature are related as $\frac{3}{2}kT = K$. This gives

$T = 1.4 \times 10^9\ \text{K}$.

With a temperature of $1.5 \times 10^7\ \text{K}$, the protons do not have enough energy to come sufficiently close for nuclear fusion to take place. But you and I are alive on the earth. This means hydrogen is indeed being converted into helium in the core of the sun. Whatever my calculations, protons do come to the femtometer range to allow nuclear forces to act. From where do they get energy to come so close to each other? There is no known source which can lend this extra energy. Once it is in the nuclear range and the deuteron is formed, the energy is the same as before, the extra energy seems to have vanished. The energy balance in the nuclear reactions described above is perfect. The apparent violation is only for a short time.

10.6 Another interpretation of energy-time uncertainty

I have given you a specific interpretation of energy-time uncertainty. The quantity ΔE is the uncertainty in energy in the given state of the system and Δt is the time in which the state evolves significantly. Now I give you another interpretation which is closely related to the position-momentum uncertainty principle.

Consider a free particle and suppose its wave function is represented by a wave packet. The momentum is distributed with a spread Δp_x and the wave packet itself is spread over a distance Δx (Fig. 10.3). Then $\Delta x\, \Delta p_x \approx \hbar$. For a free particle,

$$E = \frac{p^2}{2m}$$

or $$\Delta E = \frac{p}{m}\Delta p_x. \qquad \text{(i)}$$

This is the spread in the energy. The spread in the energy must be there, as a wave packet does not represent an energy eigenstate. In equation (i), p represents the mean value of momentum and Δp_x

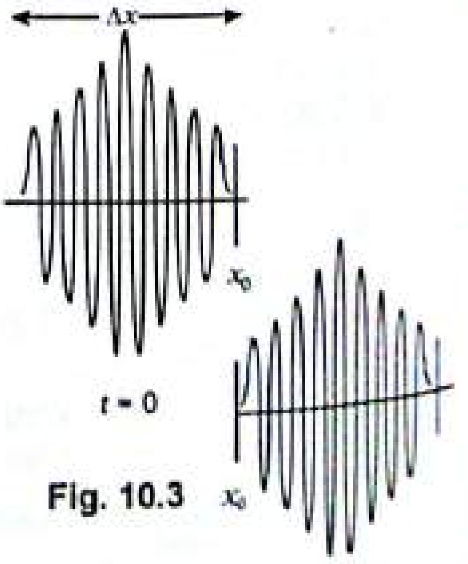


Fig. 10.3

is the spread in it. Now suppose I want to do a measurement on this particle. My measurement apparatus is at some position $x = x_0$ and the measurement is made as the particle passes through this point. But the particle is represented by the wave packet having a spread Δx in it. It will take a finite time Δt for the wave packet to pass through x_0 and for this time interval presence of the particle will be felt there. So I have a time Δt available to me to make the measurement. The wave packet as a whole moves with the group velocity given by $v_g = \frac{p}{m}$.

As the wave packet has a spread Δx, the time available for the measurement is

$$\Delta t = \frac{\Delta x}{v_g} = \frac{\Delta x}{(p/m)}.$$

Thus $(\Delta E)(\Delta t) = \left(\frac{p}{m}\Delta p_x\right)\left(\frac{\Delta x}{p/m}\right) = \Delta x\, \Delta p_x \approx \hbar$.

Remember, ΔE is the uncertainty in the energy of the particle and Δt is the time available to make measurement on this particle.

10.7 You Learned in this Chapter

- If the wave function of a particle is such that it has an uncertainty ΔE, the wave function changes appreciably in a time $\Delta t \approx \hbar/\Delta E$. The relation $\Delta E\ \Delta t \approx \hbar$ is called energy–time uncertainty relation. In this, Δt may also be interpreted as the time available to make a measurement on the particle.
- All excited states of nuclei, atoms or molecules have some energy spread. As a result, the spectral lines are never strictly monochromatic. The linewidth due to this energy uncertainty is called natural linewidth.
- The lifetime of an excited state and the energy spread in this state are related by energy–time uncertainty relation.
- Talking in the language of classical physics, an amount ΔE of energy may seem to get created or destroyed temporarily for a time $\Delta t \approx \hbar/\Delta E$.

Solved Problems

1. Gamma rays of energy $E_0 = 14.4\ \text{keV}$ are emitted when ^{57}Fe nuclei make transition from the first excited state to the ground state. The lifetime of this excited state is about $3 \times 10^{-8}\,\text{s}$. If the spread in the energy of the excited state is written as $\Delta E = \frac{v}{c}E_0$ find the value of v. Here c is the speed of light in vacuum.

Solution: $\Delta E \approx \frac{\hbar}{\tau}$.

So, $\frac{v}{c}E_0 \approx \frac{\hbar}{\tau}$

or,
$$v \approx \frac{\hbar c}{E_0\tau} = \frac{hc}{2\pi E_0\tau}$$

$$= \frac{1240\text{ eV nm}}{2\pi \times 14.4 \times 10^3\text{ eV} \times 3 \times 10^{-8}\text{ s}} \approx 0.12\text{ mm/s}.$$

2. A charged pion has rest mass energy 140 MeV and lifetime 2.6×10^{-8} s. Find the uncertainty in determination of the rest mass energy and express it as a fraction of the rest mass energy itself.

Solution: The time available for the measurement of the rest mass energy is about 2.6×10^{-8}s. The uncertainty in energy must be related to this time through the Heisenberg energy–time uncertainty principle. The energy here refers to the rest mass energy. Thus,

$$\Delta E \approx \frac{\hbar}{\Delta t}$$

$$= \frac{6.6 \times 10^{-16}\text{eV s}}{2.6 \times 10^{-8}\text{s}} \approx 2.5 \times 10^{-8}\text{eV}.$$

Thus,
$$\frac{\Delta E}{E} = \frac{2.5 \times 10^{-8}\text{eV}}{140 \times 10^6\text{eV}} \approx 1.8 \times 10^{-16}.$$

3. In one model of nuclear force between two nucleons, it is assumed that one nucleon (proton or neutron) emits a pi-meson of rest mass energy 135 MeV and other nucleon absorbs it. Estimate the range of nuclear force.

Solution: Let me assume that the nucleons are protons. You can very well take them as neutrons or one proton and one neutron. In this model when a proton emits a pi-meson, the proton remains the same proton, it does not convert to a particle of smaller mass. This means the reaction is

$$\text{p} \rightarrow \text{p} + \text{meson}. \qquad \text{(i)}$$

But this means an extra 135 MeV of energy is "created". This is an apparent violation of conservation of energy principle. However this meson gets absorbed by the other proton as the meson reaches there. This reaction is,

$$\text{p} + \text{meson} \rightarrow \text{p}. \qquad \text{(ii)}$$

Again there is an apparent violation of conservation of energy principle. But if you take (i) and (ii) together, the energy remains conserved. This means, the violation has taken place for only a time Δt taken by the meson to cover the distance between the nucleons. Quantum mechanics allows you to do so as long as $\Delta E\,\Delta t \approx \hbar$. Thus $\Delta t \approx \frac{\hbar}{\Delta E}$. How much distance can the meson travel in this time? The maximum it can go is

$$r = c\Delta t = \frac{\hbar c}{\Delta E} = \frac{1240\text{ eV nm}}{6.28 \times 135 \times 10^6\text{eV}} \approx 1.4 \times 10^{-6}\text{nm} \approx 10^{-15}\text{m}.$$

Thus the range of nuclear interaction should be about a femtometer.

EXERCISES

1. A spectral line of wavelength 600 nm has a natural linewidth of 10^{-4} nm. Estimate the lifetime of the excited state from where the transitions have taken place.
   Ans. ~ 10^{-9}s
2. A neutral pi-meson has lifetime of 4.4×10^{-24} s and a rest mass of 765 MeV. Find the ratio of the uncertainty in the rest mass energy to the rest mass energy itself.
   Ans. ~ 20 %

3. The delta particle has a rest mass energy of 1236 MeV with a spread of about 120 MeV. Estimate the lifetime of the delta particle.

Ans. 5.5×10^{-24} s

4. A free particle of mass 10^{-26} kg has wave function $\psi(x) = Ae^{-\frac{x^2}{a^2}} e^{\frac{i}{\hbar}p_0 x}$ at time $t = 0$, where $a = 0.2$ nm and $p_0 = 10^{-22}$ kg.m/s.

(a) What is $\langle p_x \rangle$?

(b) What is the uncertainty Δp_x in the momentum?

(c) What is the uncertainty ΔE in energy?

(d) At what time will the peak of the wave packet reach $x_0 = 1.2$ nm?

(e) Estimate the time Δt taken by the wave packet to pass through the point $x_0 = 1.2$ nm.

(f) Find $\Delta E \, \Delta t$.

Ans. (a) p_0 (b) $\hbar/a$ (c) 0.03 eV (d) 1.2×10^{-13}s (e) 10^{-14}s (f) 3.2×10^{-16}eV s

5. Let $|\phi_1\rangle$, $|\phi_2\rangle$ be two eigenfunctions of the Hamiltonian of a particle corresponding to the energies E_0 and $4E_0$ respectively. The wave function of the particle at time $t = 0$ is $\psi(x) = \frac{1}{\sqrt{2}}(|\phi_1\rangle + |\phi_2\rangle)$ which is an eigenfunction of an operator A with an eigenvalue a_0. This operator corresponds to an observable quantity a.

(a) What is the probability of finding the value a_0 if a measurement of a is made at time $t = 0$?

(b) What is the probability of finding the value a_0 if a measurement of a is made at time t?

(c) At what minimum time t_0 should a measurement of a be made so that the probability of finding the value a_0 is zero?

(d) Find the values of $\langle E \rangle$, $\langle E^2 \rangle$ and ΔE at time $t = 0$.

(e) Find $(\Delta E)\, t_0$.

Ans. (a) 1 (b) $\cos^2 \frac{3E_0 t}{2\hbar}$ (c) $\frac{\pi\hbar}{3E_0}$ (d) $\frac{5E_0}{2}, \frac{17E_0^2}{2}, \frac{3E_0}{2}$ (e) $\frac{\pi\hbar}{2}$

11

Probability Can Flow—Probability Current Density

If the state of a particle at a given time is described by the wave function $\psi(x)$, the probability of finding it in the range x to $x + dx$ is given by $dP = |\psi(x)|^2 \, dx$. In three dimensions, the wave function is written as $\psi(\mathbf{r})$ and the probability of finding the particle in the volume $d\tau$ at position $\mathbf{r}$ is $dP = |\psi(\mathbf{r})|^2 \, d\tau$.

The probability per unit volume is called probability density and is denoted by $\rho(\mathbf{r})$.

$$\rho(\mathbf{r}) = \frac{dP}{d\tau} = |\psi(\mathbf{r})|^2 . \tag{11.1}$$

Probability of finding the particle is a conserved quantity. If I calculate the probability of finding the particle in the whole of the space, it must be 1. As time passes, the wave function changes and the probability of finding the particle in a given volume may increase or decrease. But if the probability increases in a given volume, it must decrease in the rest of the space. In certain sense, you can imagine probability as something that can flow from one region to another.

It turns out that this concept is very useful when we describe a beam of particles moving under different force fields. Before elaborating on this, let me describe how we handle flow of matter from one region to another in fluid dynamics.

11.1 Current density in a fluid flow

Suppose a fluid flows through a region. At any point P (Figure 11.1), the fluid arrives with a velocity $\mathbf{v}$ and passes through it. Construct a small area dA around P, which is perpendicular to the velocity $\mathbf{v}$. An amount dm of the fluid crosses the area dA in time dt. We define current density $\mathbf{J}$ at the point P as

$$\mathbf{J} = \frac{dm}{(dA)(dt)}\left(\frac{\mathbf{v}}{v}\right). \tag{11.2}$$

What is $(\mathbf{v}/v)$? It is just a unit vector in the direction of the velocity at point P. The magnitude of the current density $\mathbf{J}$ is

$$J = |\mathbf{J}| = \frac{dm}{(dA)(dt)}$$

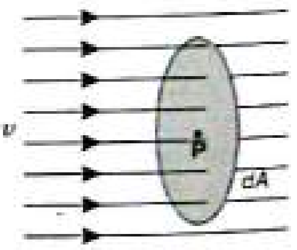


Fig. 11.1

which is the mass flowing per unit time through a unit area perpendicular to the direction of the flow. The fluid flowing through the area dA per unit time is $dm/dt = J\,dA$.

You can work out the expression for the current density in terms of the velocity $\mathbf{v}$ and the density ρ of the fluid. I have done it for you in Appendix-2. It is

$$\mathbf{J} = \rho\mathbf{v} . \tag{11.3}$$

Each of these quantities, $\mathbf{J}$, ρ and $\mathbf{v}$ can be a function of space point $\mathbf{r}$ as well as of time t. While $\rho(\mathbf{r}, t)$ gives the density of the fluid at the point $\mathbf{r}$ at time t, $\mathbf{v}(\mathbf{r}, t)$ tells how the fluid is moving there and the current density $\mathbf{J}(\mathbf{r}, t)$ tells how much of the fluid crosses per unit time through an area around $\mathbf{r}$.

Similar concept is used to define the electric current density. If there are n free electrons per unit volume in a conducting wire and the drift velocity of these electrons is v, the current density $\mathbf{J} = ne\mathbf{v}$. The quantity ne is the charge per unit volume of these free electrons and can be written as ρ. Then $J = \rho v$ as before.

Now suppose I construct an area dA which is not perpendicular to the direction of the flow (Figure 11.2). Suppose it is tilted from the perpendicular plane by an angle θ. The perpendicular to the area also makes the same angle θ with the velocity. The projection of dA on the plane perpendicular to the velocity will have an area $dA\cos\theta$. The fluid that passes through the area dA also passes through the projection $dA\cos\theta$. Thus the fluid passing through dA per unit time is

$$\frac{dm}{dt} = J(dA\cos\theta)\,. \tag{i}$$

Let me construct a vector **dA** having magnitude equal to the area dA and the direction towards the normal to the area. This area is called the *area vector* corresponding to the area dA. Equation (i) can then be written as

$$\frac{dm}{dt} = \mathbf{J}\cdot\mathbf{dA}\,. \tag{11.4}$$

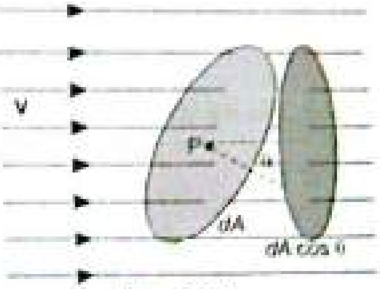


Fig. 11.2

11.1.1 Equation of continuity

Consider an imaginary closed surface S (Figure 11.3). A volume τ is bounded by this closed surface. A fluid can flow into this volume or can leave it. Consider a point P on the surface and an area dA around it. The mass of the fluid leaving the volume through this area, per unit time, is **J**.d**A** where **J** is the current density at the point P and d**A** is the vector having magnitude dA and direction towards the outward normal at P. The total mass of the fluid leaving through the entire surface S will be equal to $\oint_s \mathbf{J}\cdot d\mathbf{A}$. The circle on the integration sign tells that the integration should be performed on the whole closed surface S bounding the volume τ. Note that $\mathbf{J}\cdot\mathbf{dA}$ may be positive at some places (where the fluid is leaving) and negative at some other places (where the fluid is entering). The integration gives the net amount of fluid leaving through the entire surface.

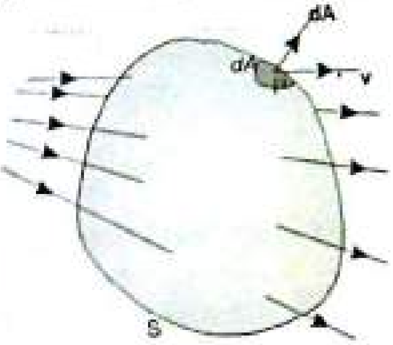


Fig. 11.3

But the total amount leaving through the entire surface should be equal to the decrease in the total mass contained in the volume τ. Thus $\oint_s \mathbf{J}\cdot\mathbf{dA}$ gives the rate of decrease of the mass in this volume. The mass of the fluid in the volume τ at time t is

$$M = \int_\tau \rho(\mathbf{r},t)\,d\tau$$

and the rate at which it goes out is $-\frac{dM}{dt}$. Thus,

$$\oint_s \mathbf{J}\cdot\mathbf{dA} = -\frac{dM}{dt} \tag{i}$$

or,

$$\oint_s \mathbf{J}\cdot\mathbf{dA} = \int_\tau -\frac{\partial}{\partial t}\rho(\mathbf{r},t)\,d\tau\,.$$

The LHS is a surface integration and the RHS is a volume integration. You might have studied in vector calculus, a theorem called *Gauss divergence theorem* which relates surface and volume integrations. Applied to the current density **J**, it is

$$\oint_S \mathbf{J}\cdot d\mathbf{A} = \int_\tau \nabla\cdot\mathbf{J}\, d\tau \tag{ii}$$

where $\nabla\cdot\mathbf{J}$, read as *divergence of* **J**, is

$$\nabla\cdot\mathbf{J} = \frac{\partial}{\partial x}J_x + \frac{\partial}{\partial y}J_y + \frac{\partial}{\partial z}J_z$$

if we use Cartesian coordinates. From (i) and (ii),

$$\int_\tau -\frac{\partial}{\partial t}\rho(\mathbf{r},t)\, d\tau = \int_\tau \nabla\cdot\mathbf{J}\, d\tau$$

or,

$$\int_\tau \left(\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{J}\right) d\tau = 0 .$$

Since this equation is valid for any volume τ,

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{J} = 0 \tag{11.5}$$

for any point **r**. Equation 11.5 is called the equation of continuity.

11.2 Probability current density

You may have guessed why I am talking so much of fluid mechanics in a book on quantum physics. The probability of finding a particle can be shown to behave like a fluid that can flow, is a conserved quantity and follows equation of continuity with proper definition of probability current density. Let me first work out the expression for probability current density in one dimension.

The probability density is

$$\rho(x,t) = |\psi(x,t)|^2 = \psi^*(x,t)\,\psi(x,t) .$$

Thus,

$$\frac{\partial\rho}{\partial t} = \frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t} .$$

Using Schrödinger equation on the RHS, the above equation becomes,

$$\begin{aligned}
\frac{\partial\rho}{\partial t} &= \left[\frac{1}{i\hbar}\mathrm{H}\psi\right]^*\psi + \psi^*\left[\frac{1}{i\hbar}\mathrm{H}\psi(x)\right] \\
&= -\frac{1}{i\hbar}\left[-\frac{\hbar^2}{2m}\psi\frac{\partial^2\psi^*}{\partial x^2} + V(x)\psi^*\psi\right] + \frac{1}{i\hbar}\left[-\frac{\hbar^2}{2m}\psi^*\frac{\partial^2\psi}{\partial x^2} + V(x)\psi^*\psi\right] \\
&= -\frac{\hbar}{2im}\left[\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right] \\
&= -\frac{\partial}{\partial x}\left[\frac{\hbar}{2im}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)\right].
\end{aligned}$$

Writing the quantity in the square bracket as J_x, the above result becomes

$$\frac{\partial\rho}{\partial t} + \frac{\partial}{\partial x}J_x = 0 .$$

This has the same structure as the equation of continuity (Equation 11.5) in one dimension. Thus

$$J_x = \frac{\hbar}{2im}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right) \tag{11.6}$$

represents the probability current density in one dimension. The corresponding expression in three dimensions is

$$\mathbf{J} = \frac{\hbar}{2im}\left[\psi^*\nabla\psi - \psi\nabla\psi^*\right] \tag{11.7}$$

where $\nabla\psi = \hat{\mathbf{i}}\frac{\partial}{\partial x}\psi + \hat{\mathbf{j}}\frac{\partial}{\partial y}\psi + \hat{\mathbf{k}}\frac{\partial}{\partial z}\psi$ is the gradient of ψ and is read as *grad* ψ. Equations 11.6 and 11.7 can also be written as

$$J_x = \frac{\hbar}{m}\operatorname{Im}\left(\psi^*\frac{\partial\psi}{\partial x}\right) \tag{11.8}$$

and

$$\mathbf{J} = \frac{\hbar}{m}\operatorname{Im}\left(\psi^*\nabla\psi\right). \tag{11.9}$$

11.3 Beam of particles

So far we have considered a single particle as our system. In many situations we work with a beam of identical particles, the particles moving one behind the other with the same velocity. For example, in a cathode ray tube electrons are continuously emitted from the electron gun and move towards the screen. In an accelerator, ions are produced at the ion source and are accelerated to a high velocity. A beam of such particles then falls on a target material where the interactions are studied. The number of particles falling on the target per unit time is called the *flux*. You can imagine any cross section in the beam and look at the number of the particles crossing through this section per unit time. That will also give the flux in the beam. Suppose the number of particles per unit length of the beam is n and each particle moves with a velocity v. What is the flux of the beam? Consider a part of the beam between the sections at A and B as shown in Figure 11.4. The particles are moving towards right. Let AB = vdt where dt denotes a small time interval. The number of particles in the beam between A and B at a given time t will be equal to $nvdt$. A particle at section A, at time t, will move through a distance vdt in the next time interval dt and reach section B. Thus all the particles which were contained in the part AB at time t, will cross through section B in the next dt. Thus the number of particles going through section B in time dt is $nvdt$ and hence per unit time this number is nv which is the flux of the beam.

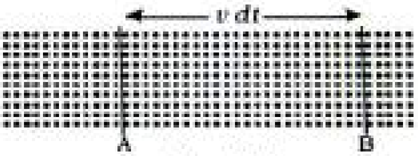


Fig. 11.4

Suppose all the particles in a beam move in the same direction and with the same momentum. Also neglect any interaction of the particles among themselves or with other objects. Then the wave functions of the particles at t = 0 may be approximated as $Ae^{i(kx+\phi)}$. The phase constant ϕ may be different for different particles having no correlation with each other. It turns out that for several calculations we can neglect the variation in ϕ and take $\psi(x) = Ae^{ikx}$ as the wave function for whole of the beam going in the positive x-direction. The probability density $|\psi(x)|^2$ is then proportional to the number of particles per unit length. The probability current density is proportional to the number of particles crossing through the given section per unit time, that is, the flux in the beam. Let me illustrate this with the help of an example.

Example 11.1

A beam of identical particles going in the x-direction is represented by the wave function

$$\psi(x,t) = Ae^{\frac{i}{\hbar}(px-Et)}.$$

Calculate the probability current density and comparing with classical expressions, check that it is proportional to the flux of the particles in the beam.

Solution: The probability current density is

$$J=\frac{\hbar}{2im}\left(\psi^{*}\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^{*}}{\partial x}\right)$$

$$=\frac{\hbar}{2im}\left[A^{*}e^{-\frac{i}{\hbar}(px-Et)}A\left(\frac{ip}{\hbar}\right)e^{\frac{i}{\hbar}(px-Et)}-Ae^{\frac{i}{\hbar}(px-Et)}A^{*}\left(-\frac{ip}{\hbar}\right)e^{-\frac{i}{\hbar}(px-Et)}\right]$$

or, $$J=|A|^{2}\frac{p}{m}. \tag{i}$$

Also, $|\psi(x,t)|^{2}=A^{*}e^{-\frac{i}{\hbar}(px-Et)}Ae^{\frac{i}{\hbar}(px-Et)}=|A|^{2}.$

Thus, $|A|^2$ is proportional to the number of particles per unit length and p/m is the velocity. The flux of the particles in the beam is nv where n is the number of particles per unit length and v is the velocity of the particles. Thus the probability current density J is proportional to the flux of the particles in the beam.

11.4 You learned in this chapter

- The probability of finding a particle is a conserved quantity. Depletion of probability in one region is accompanied by its increase in the adjacent region.
- The probability of finding a particle can be treated mathematically as a fluid which can flow and which obeys the equation of continuity.
- The flow of probability is governed by probability current density given by $J=\frac{\hbar}{2im}\left(\psi^{*}\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^{*}}{\partial x}\right)$ in one dimension and $\mathbf{J}=\frac{\hbar}{2im}\left(\psi^{*}\nabla\psi-\psi\nabla\psi^{*}\right)$ in three dimensions.
- A beam of particles can be represented by a wave function $\psi(x,t)$. The quantity $|\psi(x,t)|^2$ is interpreted as being proportional to the number of particles per unit length of the beam. The probability current density **J** then represents the flux of the particles in the beam.

Solved Problems

1. Compute the probability current density for a Gaussian wave packet $\psi(x)=Ae^{-\frac{x^2}{a^2}+\frac{i}{\hbar}p_0x}$ and compare with the classical relation $J=\rho v$.

Solution: $\psi=Ae^{-\frac{x^2}{a^2}+\frac{i}{\hbar}p_0x}.$

So, $\psi^{*}=A^{*}e^{-\frac{x^2}{a^2}-\frac{i}{\hbar}p_0x}$ and $\frac{d\psi}{dx}=A\left(-\frac{2x}{a^2}+\frac{i}{\hbar}p_0\right)e^{-\frac{x^2}{a^2}+\frac{i}{\hbar}p_0x}.$

Thus $\psi^{*}\frac{d\psi}{dx}=|A|^2\left(-\frac{2x}{a^2}+\frac{i}{\hbar}p_0\right)e^{-\frac{2x^2}{a^2}}.$

Taking complex conjugates,

$$\psi \frac{d\psi^*}{dt} = |A|^2 \left(-\frac{2x}{a^2} - \frac{i}{\hbar} p_0 \right) e^{-\frac{2x^2}{a^2}} .$$

Thus $$J = \frac{\hbar}{2im}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) = \frac{\hbar}{2im}\left(|A|^2 \frac{2ip_0}{\hbar} e^{-\frac{2x^2}{a^2}} \right) = |A|^2 e^{-\frac{2x^2}{a^2}} \frac{p_0}{m} .$$

The probability density is $\rho = \psi^* \psi = |A|^2 e^{-\frac{2x^2}{a^2}}$. Also, $\frac{p_0}{m}$ may be taken as the velocity of the wave packet. Thus J is of the form ρv. Note that all calculations are done at a given time so $\partial / \partial x$ is the same as d/dx.

2. Show that for any normalized wave packet in one dimension, $\int_{-\infty}^{\infty} J(x)\, dx = \langle p_x \rangle / m$.

Solution: $$\int_{-\infty}^{\infty} J(x)\, dx = \frac{\hbar}{2im}\left[\int_{-\infty}^{\infty} \psi^* \frac{\partial}{\partial x}\psi \, dx - \int_{-\infty}^{\infty} \psi \frac{\partial}{\partial x}\psi^* \, dx \right]$$

$$= \frac{\hbar}{2im}\left[\frac{1}{-i\hbar} \int_{-\infty}^{\infty} \psi^*(x)\left(-i\hbar \frac{d}{dx} \right)\psi(x) - \text{c.c.} \right] \qquad \text{(i)}$$

where c.c. is the complex conjugate of the first term. Remember, all operations are at a particular time t and so I am writing d/dx in place of $\partial/\partial x$. Now the integral in (i) is nothing but $\langle p_x \rangle$ which must be real. So the first term in the square bracket is $\frac{1}{-i\hbar}\langle p_x \rangle$ and hence its complex conjugate is $\frac{1}{i\hbar}\langle p_x \rangle$.

Thus $$\int_{-\infty}^{\infty} J(x)\, dx = \frac{\hbar}{2im}\left[\frac{2}{-i\hbar}\langle p_x \rangle \right] = \frac{\langle p_x \rangle}{m} .$$

3. A wave function $\psi(x)$ can be written as a superposition of two wave functions $\psi_1(x) = A_1 e^{ikx}$ and $\psi_2(x) = A_2 e^{-ikx}$ where A_1 and A_2 are real constants. Let $\rho(x)$, $\rho_1(x)$ and $\rho_2(x)$ be the probability densities and $J(x)$, $J_1(x)$ and $J_2(x)$ be the probability current densities corresponding to the wave functions $\psi(x)$, $\psi_1(x)$ and $\psi_2(x)$ respectively. Show that $J(x) = J_1(x) + J_2(x)$ but $\rho(x) \neq \rho_1(x) + \rho_2(x)$.

Solution: $\psi(x) = \psi_1(x) + \psi_2(x)$ and $J(x) = \frac{\hbar}{m}\operatorname{Im}\left(\psi^* \frac{d\psi}{dx} \right)$.

The wave function is given at a particular time. Hence I have used the symbol d/dx. Now,

$$\psi^* \frac{d\psi}{dx} = \left(\psi_1^* + \psi_2^* \right)\left(\frac{d\psi_1}{dx} + \frac{d\psi_2}{dx} \right)$$

$$= \psi_1^* \frac{d\psi_1}{dx} + \psi_2^* \frac{d\psi_2}{dx} + \psi_1^* \frac{d\psi_2}{dx} + \psi_2^* \frac{d\psi_1}{dx} .$$

Thus $$J(x) = \frac{\hbar}{m}\operatorname{Im}\left(\psi_1^* \frac{d\psi_1}{dx} + \psi_2^* \frac{d\psi_2}{dx} \right) + \frac{\hbar}{m}\operatorname{Im}\left(\psi_1^* \frac{d\psi_2}{dx} + \psi_2^* \frac{d\psi_1}{dx} \right)$$

$$= J_1(x) + J_2(x) + \frac{\hbar}{m}\operatorname{Im}\left(\psi_1^* \frac{d\psi_2}{dx} + \psi_2^* \frac{d\psi_1}{dx} \right).$$

Let me evaluate the part in the bracket.

$$\psi_1^*(x) = A_1 e^{-ikx}, \quad \frac{d\psi_2}{dx} = -ikA_2 e^{-ikx}, \quad \psi_2^*(x) = A_2 e^{ikx} \quad \text{and} \quad \frac{d\psi_1}{dx} = A_1 ik e^{ikx}$$

Thus $$\psi_1^* \frac{d\psi_2}{dx} + \psi_2^* \frac{d\psi_1}{dx} = -ikA_1A_2e^{-2ikx} + ikA_1A_2e^{2ikx} = A_1A_2ik(\sin 2kx)(2i) = -2A_1A_2k(\sin 2kx).$$

Its imaginary part is zero and hence $J(x) = J_1(x) + J_2(x)$.

The probability density is

$$\begin{aligned}\rho(x) = \psi^*(x)\psi(x) &= \left(\psi_1^* + \psi_2^*\right)(\psi_1 + \psi_2)\\ &= \psi_1^*\psi_1 + \psi_2^*\psi_2 + \psi_1^*\psi_2 + \psi_2^*\psi_1\\ &= \rho_1(x) + \rho_2(x) + \left[\psi_1^*\psi_2 + \psi_2^*\psi_1\right].\end{aligned}$$

Now $$\psi_1^*\psi_2 = A_1e^{-ikx}A_2e^{-ikx} = A_1A_2e^{-2ikx}$$

and $$\psi_2^*\psi_1 = A_2e^{ikx}A_1e^{ikx} = A_1A_2e^{2ikx}.$$

Thus the term in the square bracket is,

$$A_1A_2\left(e^{2ikx} + e^{-2ikx}\right) = A_1A_2\, 2\cos(2kx).$$

This is not zero for all x. So $\rho(x) \neq \rho_1(x) + \rho_2(x)$.

EXERCISES

1. What is the SI unit of probability current density in one dimension? In three dimensions? **Ans.** s^{-1}, $m^{-2}s^{-1}$
2. Two separate beams of identical particles are described by the wave functions, $\psi_1 = A_1e^{ik_1x}$ and $\psi_2 = A_2e^{ik_2x}$. Find the ratio of the flux of particles in the first beam to the second beam. **Ans.** $\frac{|A_1|^2 k_1}{|A_2|^2 k_2}$
3. A beam of electrons and a beam of protons are described by the same wave function $\psi(x) = Ae^{ikx}$. Find the ratio of the flux of the electron beam to the flux of the proton beam. **Ans.** 1836
4. The wave function of a beam of particle in a certain region is described by $\psi(x) = A\left[e^{ikx} + 4e^{-ikx}\right]$. (a) Find the probability current density $J(x)$. (b) Find the ratio of the number of particles going in the positive x-direction to those going in the negative x-direction. **Ans.** (a) $-15|A|^2\hbar k/m$ (b) 1/16
5. Calculate the probability current density **J** for a three-dimensional wave function $\psi(\mathbf{r}) = (A/r)e^{ikr}$. Use $\nabla\psi = \frac{\partial}{\partial r}\hat{\mathbf{r}} + \frac{1}{r}\frac{\partial}{\partial\theta}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\hat{\boldsymbol{\varphi}}$ which is the expression for $\nabla\psi$ in spherical polar coordinates. **Ans.** $|A|^2\left(\frac{\hbar k}{m}\right)\frac{1}{r^2}\hat{r}$

6. The wave function of a particle is given by $\psi(x) = \frac{1}{\sqrt{a}} \exp\left(-\frac{|x|}{a} + \frac{i}{\hbar} p_0 x \right)$. Find the probability current density $J(x)$ for $x < 0$ and also for $x > 0$. Show that it is continuous everywhere although $\psi(x)$ is not differentiable at $x = 0$. **Ans.** $\frac{p_0 e^{-2|x|/a}}{am}$ for all x

7. The wave function of a particle is $\psi(x) = A\cos kx$. Show that the probability current is zero everywhere. Explain your result on physical grounds.

8. The wave function of a particle is $\psi(x) = Ae^{ikx} + Be^{-ikx}$ for $x < 0$ and $\psi(x) = Ce^{ik'x}$ for $x > 0$. Here k and k' are real and the potential do not make any infinite jump. (b) Show that the probability current density is same everywhere. (a) Find $|A/C|$ and $|B/C|$ in terms of k and k'. **Ans.** $\frac{1}{2}\left(1 + \frac{k'}{k}\right), \frac{1}{2}\left(1 - \frac{k'}{k}\right)$

9. Show that if the wave function of a particle is real, its average momentum must be zero.

12

Bound States of a Particle — Deep Square Well Potential

12.1 Time independent Schrödinger equation

By now you must have realized how important are the eigenvalues and eigenfunctions of the operator Hamiltonian in describing the dynamics of a given system. The eigenfunctions $|\phi_i\rangle$ represent very special states in which all measurable quantities of the system remain constant as time passes. The eigenvalues E_i of the Hamiltonian represent the possible values of the energy of the system which an energy measurement can give. The eigenfunctions $|\phi_i\rangle$ and the eigenvalues E_i also play key role in the time evolution of the state of the system as you have seen earlier. You remember, in Chapter-9 we described how to solve the Schrödinger equation

$$\mathrm{H}|\psi\rangle = i\hbar\frac{\partial}{\partial t}|\psi\rangle .$$

The solution was written in terms of energy eigenvalues and eigenfunctions. And how do I get the energy eigenvalues E_i and energy eigenfunctions $|\phi_i\rangle$ for a system? This I obtain from the eigenvalue equation for the Hamiltonian

$$\mathrm{H}|\phi\rangle = E|\phi\rangle . \tag{12.1}$$

This equation is called the *time independent Schrödinger Equation*. In this chapter and the next few chapters I will discuss different physical situations and solve this equation for those situations.

12.2 Bound state potentials

A particle not interacting with any of the surrounding bodies is called a free particle. But often there are forces on the particle and the motion of the particle is governed by these forces. For conservative forces, one defines potential energy $V(x)$ (in one dimension). In quantum mechanics we do not talk in terms of forces, rather we talk in terms of the potential energy. And you remember, quantum physicists call it potential. The Hamiltonian of a particle subjected to a potential $V(x)$ is written as

$$\mathrm{H} = \mathrm{K} + \mathrm{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

and the time independent Schrödinger Equation is

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

The possible solutions of this differential equation subject to the conditions for a realistic wave function give the energy eigenvalues E_i and eigenfunctions $\phi_i(x)$.

Different situations of interest may be grouped into two categories. In one, the eigenfunction is confined to a finite region, outside which its absolute value $|\phi_i(x)|$ drops rapidly. Such states are called *bound states*, and potentials $V(x)$ capable of producing bound states are called *bound state potentials*. In the other category, the eigenfunction extends to infinite region. Such states are called *unbound state*. In this chapter, I shall discuss a simple case of bound state.

In classical mechanics, a bound state results when

(a) the potential $V(x)$ has a minimum as you plot it, and

(b) the total energy E of the particle is larger than the minimum, but lower than any maximum on either side of the minimum. In such a case, if you draw a line parallel to the x-axis at this energy, it will cut the $V(x)$ curve at two points above the minimum.

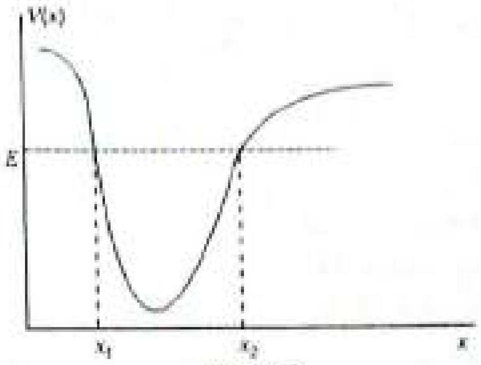


Fig. 12.1

Figure 12.1 shows a typical case of bound state potential. The particle is confined to the range x_1 to x_2. At any point outside this range, the total energy E is less than the potential energy V and this would require the kinetic energy $K = E - V$ to be negative. And that is unacceptable in classical physics.

In quantum mechanics also, the potential $V(x)$ should have a minimum in order to produce a bound state. However, in this case, there are some major differences in the behavior of the particle as compared to what we have in classical mechanics. I wish to focus your attention to these interesting differences and hence wish to keep the mathematical complexities at the minimum. I will therefore start with a class of simple potential functions called *square well potentials*. In these, the potential function is constant in a certain range, jumps suddenly to some other value and remains constant again in a certain region and so on. Figure 12.2 shows some examples of a square well potential.

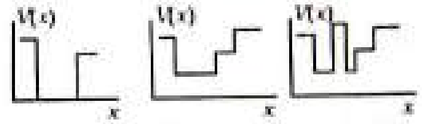


Fig. 12.2

Though a sudden jump in potential from a value V_1 to another value V_2 is not realistic, it is not difficult to arrange for a steep change in potential. Look at the gravitational potential energy of a ball falling in a tumbler from its edge. As the ball falls, the potential energy decreases by *mgh* in a very small horizontal length. Steep changes in potential can also occur for quantum systems. When two wires of different materials are joined, a potential difference is developed across the junction. As an electron moves from one wire to the other it encounters a steep change in potential energy.

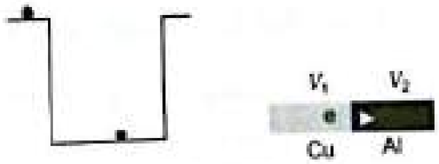


Fig. 12.3

12.3 Boundary conditions at a sudden potential jump

You know that any meaningful wave function of a particle must satisfy certain conditions such as

(a) It should be continuous everywhere. For any point x_0,

$$\underset{\varepsilon \to 0}{\mathrm{Lt}}\ \psi(x_0 - \varepsilon) = \underset{\varepsilon \to 0}{\mathrm{Lt}}\ \psi(x_0 + \varepsilon).$$

(b) It should be finite at all points in space.

(c) It should be square integrable.

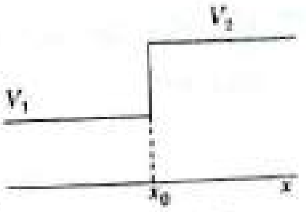


Fig. 12.4

These conditions come from the Born interpretation of $\psi(x)$ in terms of the probability of finding the particle in a given region and have to be satisfied in all conditions, even if the potential jumps suddenly (Figure 12.4).

Apart from these, there is some restriction on the slope $d\psi/dx$. I will show that it should be continuous everywhere, unless there is an infinite jump in the potential. I will do this for the stationary state $\phi_i(x)$ which is quite sufficient because any wave function can be written as a linear combination of these $\phi_i(x)$.

A stationary state wave function $\phi(x)$ satisfies

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

or, $$-\frac{\hbar^2}{2m}\int_{x_0}^{x_0+\varepsilon}\frac{d^2\phi}{dx^2}\,dx = \int_{x_0}^{x_0+\varepsilon}[E-V(x)]\,\phi(x)\,dx$$

or, $$-\frac{\hbar^2}{2m}\left[\frac{d\phi}{dx}\right]_{x_0}^{x_0+\varepsilon} = \int_{x_0}^{x_0+\varepsilon}[E-V(x)]\,\phi(x)\,dx$$

where x_0 is any particular value of x and ε is an infinitesimally small quantity. Now suppose $V(x)$ changes by at most a finite value at $x = x_0$. Each of E, $V(x)$ and $\phi(x)$ is then finite and hence $[E-V(x)]\phi(x)$ will have some maximum absolute value λ_m in the range x_0 to $x_0+\varepsilon$. The integration on the right hand side is therefore less than $\varepsilon\lambda_m$ in magnitude and will go to zero as ε goes to zero. Thus

$$-\frac{\hbar^2}{2m}\left[\frac{d\phi}{dx}\right]_{x_0}^{x_0+\varepsilon} \to 0 \quad \text{as } \varepsilon \to 0$$

or $$\left[\frac{d\phi}{dx}\right]_{x_0} = \underset{\varepsilon\to 0}{\text{Lt}}\left[\frac{d\phi}{dx}\right]_{x_0+\varepsilon}.$$

Similarly, by integrating equation (i) from $x_0-\varepsilon$ to x_0, you can show,

$$\left[\frac{d\phi}{dx}\right]_{x_0} = \underset{\varepsilon\to 0}{\text{Lt}}\left[\frac{d\phi}{dx}\right]_{x_0-\varepsilon}.$$

So, the left hand limit, the right hand limit and the value, all are same at $x = x_0$. This means $\frac{d\phi}{dx}$ must be continuous at x_0. I have assumed that $V(x)$ remains finite in the range $x_0-\varepsilon$ to $x_0+\varepsilon$. If the potential jumps at $x = x_0$ by an infinite amount, the above assumption is not valid and the continuity of $\frac{d\phi}{dx}$ is not guaranteed. Thus the fourth condition on the wave function is the following:

(d) The slope of the wave function is continuous at all points where the potential is continuous or makes a finite jump.

The conditions (a) to (d) are called the boundary conditions on the wave function.

12.4 Infinite square well potential

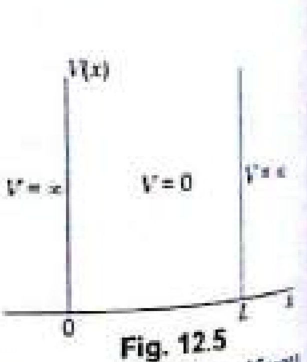


Fig. 12.5

A very simple square well potential is given as

$V(x) = \infty$ for $x < 0$

$= 0$ for $0 < x < L$

$= \infty$ for $x > L$.

The potential is zero in the region $0 < x < L$ and is infinity everywhere else. This is called an *infinite square well potential* or *deep square well potential*. It is also called a *box potential* and the situation is called *particle in a one-dimensional box*. The name comes from the usual property of a box to keep things within. If you place a ball in a rigid box, the ball can move anywhere inside the box but cannot come out. If it tries to come out through a wall, the wall exerts a large force to send it back into the box. It needs infinite amount of work to penetrate the rigid wall, hence we say that if the ball penetrates and goes out, its potential energy becomes infinite (another way of saying that it never goes out). Our one-dimensional box potential becomes infinite at $x = 0$ and at $x = L$. The particle is confined in the range $0 < x < L$ and cannot cross through the end points. In the range $0 < x < L$, the potential energy is constant (zero) implying that the particle can freely move in this region. Thus it acts like a one-dimensional box.

12.4.1 Energy eigenvalues and eigenfunctions

The Schrödinger Equation for the region $0 < x < L$ (inside the well) is

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

or $$\frac{d^2\phi}{dx^2} + k^2\phi = 0 \quad \text{where} \quad k = +\sqrt{\frac{2mE}{\hbar^2}}\,.$$

You must have encountered such a differential equation in many contexts. One is simple harmonic motion of a spring-mass system. The solution of this equation is

$$\phi(x) = A\sin(kx + \varepsilon) \quad \text{for } 0 < x < L\,. \qquad \text{(i)}$$

For $x < 0$ and $x > L$, the wave function must be zero, because there is no chance of finding the particle in these regions.

$$\phi(x) = 0 \quad \text{for} \quad x < 0 \text{ and } x > L\,. \qquad \text{(ii)}$$

Now apply the boundary condition that $\phi(x)$ should be continuous everywhere. Doing this at $x = 0$, from (i) and (ii),

$$0 = A\sin\varepsilon\,. \qquad \text{(iii)}$$

Can I take $A = 0$? If I do that, the wave function will be zero everywhere. If the particle is there, the wave function should be nonzero at least somewhere, making $A = 0$ unacceptable. Thus from (iii),

$$\varepsilon = 0$$

and the eigenfunction in (i) becomes

$$\phi(x) = A\sin kx \quad \text{for } 0 < x < L\,. \qquad \text{(iv)}$$

Now apply the condition that the wave function should be continuous at $x = L$. From (iv) and (ii),

$$\sin kL = 0$$

or $$kL = n\pi, \text{ where } n = 1, 2, \ldots$$

We do not take $n = 0$, because that will give $k = 0$ and that will again make the eigenfunction zero everywhere (check from (iv) above). Also I have not included negative integral values of n because $\phi(x)$ obtained by using these will differ from those obtained with positive n only by an overall multiplication by -1 which will not give any different state of the system. Thus

$$k = \frac{n\pi}{L}\,,\ n = 1, 2, \ldots \qquad (12.2)$$

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

or $$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}, \quad n = 1, 2, 3, \ldots \qquad (12.3)$$

I have put the subscript n to write the energy eigenvalues to clearly identify different eigenvalues. These are the only possible values of energy for a particle trapped in a deep square well potential. The lowest energy

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

is called the *ground state energy* and other energies are the *excited state energies*. The eigenfunctions as given by equations (iv) and (ii) above are,

$$\phi_n(x) = A_n \sin\frac{n\pi x}{L} \quad \text{for} \quad 0 < x < L$$
$$= 0 \qquad \text{otherwise.}$$

The normalization constant A_n can be obtained from the requirement that

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

This gives $|A_n|^2 = \frac{2}{L}$. Choosing real positive value, $A_n = \sqrt{\frac{2}{L}}$. Thus, the eigenfunctions of the Hamiltonian are

$$\begin{aligned} \phi_n(x) &= \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L} \quad \text{for} \quad 0 < x < L \\ &= 0 \qquad\qquad\qquad\quad \text{otherwise} \end{aligned} \tag{12.4}$$

for $n = 1, 2, 3, \ldots$.

So the minimum energy of the particle in a deep square well potential is E_1 (Equation 12.3). If the particle has this energy, its wave function will be $\phi_1(x)$ (Equation 12.4). Similarly if the particle has energy E_n, its wave function will be $\phi_n(x)$. Remember, it is not necessary that the wave function of the particle is one of the energy eigenfunctions. It can be a superposition of the energy eigenfunctions. In that case the energy of the particle will not be definite.

Figure 12.6 shows some of the energy eigenfunctions, the probability densities $|\phi_n(x)|^2$ and the eigenvalues graphically. For the lowest energy state, the wave function vanishes at the ends and is maximum at the middle. This means the particle has maximum probability of being found at the middle. On the other hand, the wave function vanishes at the middle for the first excited state. Thus the particle will never be found at $x = L/2$ in the first excited state.

Note that the slope $\frac{d\phi}{dx}$ is discontinuous at $x = 0$ and $x = L$. This is because the potential jumps by infinite amount at these points.

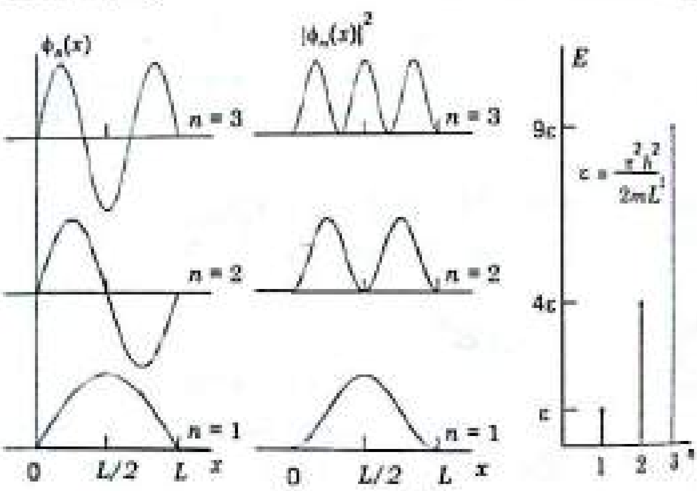


Fig. 12.6

The allowed energy increases in proportion to n^2 as one goes for the excited states.

Orthogonality

You can check explicitly that different energy eigenfunctions are orthogonal to each other.

$$\begin{aligned} \langle \phi_m | \phi_n \rangle = \int_{-\infty}^{\infty} \phi_m^*(x)\, \phi_n(x) dx &= \frac{2}{L}\int_0^L \sin\frac{m\pi x}{L} \sin\frac{n\pi x}{L}\, dx \\ &= \frac{1}{L}\int_0^L \left[\cos\frac{(m-n)\pi x}{L} - \cos\frac{(m+n)\pi x}{L}\right] dx \\ &= \frac{1}{L}\left[\frac{\sin\frac{(m-n)\pi x}{L}}{\frac{(m-n)\pi}{L}}\Bigg|_0^L - \frac{\sin\frac{(m+n)\pi x}{L}}{\frac{(m+n)\pi}{L}}\Bigg|_0^L \right]. \end{aligned}$$

As the sin function is zero for any integral multiple of π, all four terms involved in the above expression are zero unless $m = n$. Hence $\langle \phi_m | \phi_n \rangle = 0$ if $m \neq n$.

It is useful to remember (m, n integers)

$$\int_0^L \sin\frac{m\pi x}{L}\sin\frac{n\pi x}{L}\,dx = 0 \text{ if } m \neq n$$

and
$$\int_0^L \sin^2\frac{m\pi x}{L}\,dx = \frac{L}{2}.$$

These equations may be combined in the following form.

$$\int_0^L \sin\frac{m\pi x}{L}\sin\frac{n\pi x}{L}\,dx = \frac{L}{2}\delta_{mn}.$$

12.4.2 Comparison with classical mechanics

(a) There is a minimum energy

In classical mechanics there is no restriction on minimum energy. You can put the particle at rest in the box giving zero energy. But quantum mechanics does not allow the particle to have energy less than the ground state energy E_1. The reason of this can be traced in the uncertainty principle. As the particle can be found in the range $0 < x < L$, the uncertainty Δx in its position is of the order of L. The linear momentum is then uncertain by at least an amount $\hbar/L$. This means we cannot say that the particle is at rest. So there should be a minimum energy.

Example 12.1

A particle of mass 1 g is confined in a box of length 1 cm. What could be the minimum kinetic energy of the particle?

Solution: The minimum kinetic energy is the same as the minimum total energy if we take the potential energy to be zero inside the box. Thus the minimum kinetic energy of the particle is

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2} \approx 5 \times 10^{-61}\text{ J}.$$

The situation given in the above example suits the description by classical mechanics. You can never measure energies of the order of 10^{-61} J with the present day technology. It is as good as no restriction on the minimum energy and classical mechanics is good enough to deal with such cases.

(b) Energy values are discrete

The allowed energies of a particle in a deep potential well are seen to be discrete. If you measure the energy, it is either E_1, or E_2, or E_3, and so on. Classically, the energy can take any value but quantum mechanically not all values are allowed. This is a general property of bound states in quantum mechanics.

(c) Nodes in eigenfunctions

For any given eigenfunction, there are certain values of x where the function is zero. These values or points are called nodes. The points $x = 0$ and $x = L$ are nodes for all eigenfunctions $\phi_n(x)$. Apart from these, there is no node in the ground state, one node in the first excited state, two nodes in the second excited state and so on. The number of nodes increases, as we go for higher energy eigenfunctions. This is a general phenomenon in bound states.

12.4.3 Mean values and uncertainties

Suppose the particle is in the stationary state $|\phi_n\rangle$. Let us calculate the mean values of position and momentum and their uncertainties.

(a) Position

The probability density $|\phi_n(x)|^2 = \frac{2}{L}\sin^2\frac{n\pi x}{L}$ is symmetric about $x = L/2$ (Figure 12.6). Hence the mean value of x is $\langle x\rangle = L/2$. We can verify it by actual calculation.

$$\langle x\rangle = \int_{-\infty}^{\infty}\phi_n^*(x)\,x\,\phi_n(x)\,dx = \int_0^L\frac{2}{L}x\sin^2\frac{n\pi x}{L}\,dx = \frac{L}{2}.$$

Also $$\langle x^2\rangle = \int_{-\infty}^{\infty}\phi_n^*(x)\,x^2\,\phi_n(x)\,dx = \frac{2}{L}\int_0^L x^2\sin^2\frac{n\pi x}{L}\,dx = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}.$$

The uncertainty in position is

$$\Delta x = \left[\langle x^2\rangle - \langle x\rangle^2\right]^{1/2} = L\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}.$$

(b) Momentum

The momentum operator is $P_x = -i\hbar\frac{d}{dx}$. The average value of the momentum in the state $\phi_n(x)$ is

$$\langle p_x\rangle = \int_{-\infty}^{\infty}\phi_n^*(x)\left[-i\hbar\frac{d}{dx}\right]\phi_n(x)\,dx = -\left(\frac{2}{L}\right)(i\hbar)\frac{n\pi}{L}\int_0^L\sin\frac{n\pi x}{L}\cos\frac{n\pi x}{L}\,dx = 0$$

and that of p_x^2 is

$$\langle p_x^2\rangle = \int_{-\infty}^{\infty}\phi_n^*(x)\left[-\hbar^2\frac{d^2}{dx^2}\right]\phi_n(x)\,dx = \frac{2}{L}\hbar^2\left(\frac{n\pi}{L}\right)^2\int_0^L\sin^2\frac{n\pi x}{L}\,dx = \frac{n^2\pi^2\hbar^2}{L^2}.$$

The uncertainty in the momentum is

$$\Delta p_x = \left[\langle p_x^2\rangle - \langle p_x\rangle^2\right]^{1/2} = \frac{n\pi\hbar}{L}.$$

The uncertainty product is

$$\Delta x\,\Delta p_x = n\pi\hbar\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}.$$

For $n = 1$, that is for the ground state, it is about $0.57\,\hbar$. You must be happy to see that it is more than $\hbar/2$. For higher energy states the uncertainty product is still higher.

12.5 Density of State

The energy eigenvalues of a particle in an infinite deep square well potential are given by

$$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}\quad,\quad n = 1, 2, 3, \ldots \tag{i}$$

Each eigenvalue is nondegenerate and hence there is one quantum state corresponding to each of the allowed energy values. If L is very large, the successive energy values differ by only a small amount and in certain cases it may be useful to treat them as almost continuous. We then ask the question "how many quantum states (energy eigenstates) are there in the energy interval E to $E + dE$". If this number is dN, the quantity dN/dE is called the *density of states* or, in short, DOS. Often the number of quantum states in the energy interval E to $E + dE$ is written as $g(E)\,dE$. So $dN = g(E)\,dE$ and hence the density of states is $g(E)$.

To count the number of states (energy eigenstates) in a given energy interval, let me write the energy eigenvalues given in (i) as

$$E=\frac{\hbar^2k^2}{2m} \quad \text{where } k=\frac{n\pi}{L}.$$

Thus, k can take values $\frac{\pi}{L},\frac{2\pi}{L},\frac{3\pi}{L},\ldots\ldots$, and for each value of k, there is one quantum state which is an energy eigenfunction. I show this graphically in Figure 12.7. What I have drawn is a k-line. Like the number line that you may have learned in your primary classes, it is a k-line and at values $\frac{\pi}{L},\frac{2\pi}{L}$, etc., I have put a fat dot indicating the presence of an energy eigenstate. As our space is assumed to be one-dimensional, k-line can also be called k-space. Keep in mind that we are considering a case when L is very large, π/L is very small and energy eigenstates appear almost continuously as you move in the k-space.

Fig. 12.7

As $$k=\sqrt{\frac{2mE}{\hbar^2}}$$

$$dk=\sqrt{\frac{2m}{\hbar^2}}\frac{1}{2\sqrt{E}}dE=\sqrt{\frac{m}{2\hbar^2}}E^{-1/2}dE. \tag{ii}$$

The energy interval E to $E+dE$ corresponds to the interval k to $k+dk$ in the k-space. So, the number of states in the energy interval E to $E+dE$ is the same as the number of states in the interval k to $k+dk$ in the k-space. But in the k-space, energy eigenstates are equi-spaced at an interval of π/L. Thus the number of states in the energy interval E to $E+dE$ is

$$dN=\frac{dk}{(\pi/L)}=\frac{\left(\sqrt{\frac{m}{2\hbar^2}}E^{-1/2}dE\right)}{(\pi/L)}=L\sqrt{\frac{m}{2\hbar^2\pi^2}}\;E^{-1/2}\,dE$$

or, $$\frac{1}{L}\frac{dN}{dE}=\sqrt{\frac{m}{2\hbar^2\pi^2}}E^{-1/2}. \tag{12.5}$$

The density of states per unit length is therefore proportional to $E^{-1/2}$. Figure 12.8 shows this graphically. The density of states decreases as you consider higher and higher energies. You can easily see why it is so. The energy eigenvalues are proportional to n^2. As you consider higher values of n, the difference $(n+1)^2-n^2=2n+1$ keeps on increasing and so the spacing between energy eigenvalues increases.

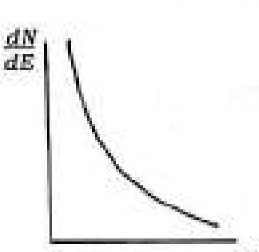


Fig. 12.8

12.6 You learned in this chapter

- The eigenvalue equation $H|\phi\rangle=E|\phi\rangle$ for the Hamiltonian is called the time independent Schrödinger equation.
- The wave function $\phi(x)$ is continuous and finite everywhere. Unless there is an infinite jump in the potential, its slope $d\phi/dx$ is also continuous.
- A bound state can appear if the potential passes through a minimum.
- Bound state energies are discrete.
- For deep square well potential with rigid walls at $x=0$ and $x=L$ the energy eigenvalues are given by $E_n=\frac{\pi^2\hbar^2n^2}{2mL^2}$ and the energy eigenfunctions by

$$\phi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \quad \text{for} \quad 0 < x < L \text{ and 0 otherwise.}$$

- For a deep square well potential with rigid walls at $x = 0$ and $x = L$,

$$\langle x\rangle = L/2, \quad \Delta x = L\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}} \quad , \quad \langle p_x\rangle = 0, \quad \Delta p_x = \frac{n\hbar\pi}{L}.$$

Solved Problems

1. A particle in a deep square well potential extending from $x = 0$ to $x = L$ has a wave function $\psi(x) = \frac{1}{\sqrt{5}}\left[|\phi_1\rangle + 2|\phi_2\rangle\right]$ where $|\phi_1\rangle$ and $|\phi_2\rangle$ denote the ground state and the first excited state wave functions. Find the expectation value of x in this state.

Solution:

$$\langle x\rangle = \langle\psi|X|\psi\rangle$$

$$= \frac{1}{\sqrt{5}}\left(\langle\phi_1| + 2\langle\phi_2|\right)X\frac{1}{\sqrt{5}}\left(|\phi_1\rangle + 2|\phi_2\rangle\right)$$

$$= \frac{1}{5}\left[\langle\phi_1|X|\phi_1\rangle + 2\langle\phi_1|X|\phi_2\rangle + 2\langle\phi_2|X|\phi_1\rangle + 4\langle\phi_2|X|\phi_2\rangle\right].$$

Now, $\langle\phi_1|X|\phi_1\rangle$ and $\langle\phi_2|X|\phi_2\rangle$ are average values of x in the states $|\phi_1\rangle$ and $|\phi_2\rangle$, and you know each of them is $L/2$. $\langle\phi_1|X|\phi_2\rangle$ and $\langle\phi_2|X|\phi_1\rangle$ are complex conjugate of each other. The wave functions $\phi_1(x)$, $\phi_2(x)$ as well as the operator X are all real. So $\langle\phi_1|X|\phi_2\rangle = \langle\phi_2|X|\phi_1\rangle$.

Thus

$$\langle x\rangle = \frac{1}{5}\left[\frac{5L}{2} + 4\langle\phi_1|X|\phi_2\rangle\right] \qquad \text{(i)}$$

Now,

$$\langle\phi_1|X|\phi_2\rangle = \int_0^L\left(\sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}\right)x\left(\sqrt{\frac{2}{L}}\sin\frac{2\pi x}{L}\right)dx$$

$$= \frac{1}{L}\int_0^L x\left(\cos\frac{\pi x}{L} - \cos\frac{3\pi x}{L}\right)dx$$

$$= \frac{1}{L}\left(-\frac{2L^2}{\pi^2} + \frac{2L^2}{9\pi^2}\right) = -\frac{16L}{9\pi^2}.$$

Putting in (i), $\langle x\rangle = \frac{L}{2} - \frac{64L}{45\pi^2}$.

2. Calculate $\langle p_x\rangle$ for $\psi(x) = \frac{1}{\sqrt{2}}\left(|\phi_1\rangle + |\phi_2\rangle\right)$ where $|\phi_1\rangle$ and $|\phi_2\rangle$ are the ground state and the first excited state wave functions of a particle in a deep square well potential.

Solution: $\psi(x) = \frac{1}{\sqrt{2}}\left(|\phi_1\rangle + |\phi_2\rangle\right)$.

So, $\langle p_x\rangle = \langle\psi|P_x|\psi\rangle$

$$= \frac{1}{\sqrt{2}}\left(\langle\phi_1| + \langle\phi_2|\right)\mathrm{P_x}\,\frac{1}{\sqrt{2}}\left(|\phi_1\rangle + |\phi_2\rangle\right)$$

$$= \frac{1}{2}\left[\langle\phi_1|\mathrm{P_x}|\phi_1\rangle + \langle\phi_2|\mathrm{P_x}|\phi_1\rangle + \langle\phi_1|\mathrm{P_x}|\phi_2\rangle + \langle\phi_2|\mathrm{P_x}|\phi_2\rangle\right]. \qquad \text{(i)}$$

Now, $\langle\phi_1|\mathrm{P_x}|\phi_1\rangle$ and $\langle\phi_2|\mathrm{P_x}|\phi_2\rangle$ are the expectation values of momentum in the ground state and in the first excited state and are zero. The other terms in (i) may be evaluated as follows.

$$\langle\phi_2|\mathrm{P_x}|\phi_1\rangle = \int_{-\infty}^{\infty}\phi_2^*(x)\left(-i\hbar\frac{d}{dx}\right)\phi_1(x)\,dx$$

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

$$= \frac{-i\hbar\pi}{L^2}\int_0^L 2\sin\frac{2\pi x}{L}\cos\frac{\pi x}{L}\,dx$$

$$= \frac{-i\hbar\pi}{L^2}\int_0^L\left(\sin\frac{3\pi x}{L} + \sin\frac{\pi x}{L}\right)dx = -\frac{8i\hbar}{3L}.$$

Also, $\langle\phi_1|\mathrm{P_x}|\phi_2\rangle = \langle\phi_2|\mathrm{P_x}|\phi_1\rangle^* = \frac{8i\hbar}{3L}$

So by (i), $\langle p_x\rangle = 0$.

If you had solved the problems of the previous chapter carefully you could have answered this problem straightaway. The wave function $\psi(x)$ is real and so $\langle p_x\rangle$ must be zero.

3. Let $|\phi_m\rangle$, $|\phi_n\rangle$ denote two energy eigenstates of a particle in a deep square well potential of width L. Prove that

$$\langle\phi_m|\mathrm{P_x^2}|\phi_n\rangle = \frac{n^2\pi^2\hbar^2}{L^2}\delta_{mn}.$$

Solution:

$$\langle\phi_m|\mathrm{P_x^2}|\phi_n\rangle = \int_{-\infty}^{\infty}\phi_m^*(x)\left[-i\hbar\frac{d}{dx}\right]\left[-i\hbar\frac{d}{dx}\right]\phi_n(x)\,dx$$

$$= \int_0^L\sqrt{\frac{2}{L}}\sin\frac{m\pi x}{L}\left(-\hbar^2\frac{d^2}{dx^2}\right)\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\,dx$$

$$= \frac{n^2\pi^2\hbar^2}{L^2}\frac{2}{L}\int_0^L\sin\frac{m\pi x}{L}\sin\frac{n\pi x}{L}\,dx = \frac{n^2\pi^2\hbar^2}{L^2}\delta_{mn}.$$

Note that the $\frac{d^2}{dx^2}\phi_n(x)$ itself is infinity at $x = 0$ and $x = L$. But its integral across these points is finite and multiplying by $\phi_n(x)$ itself makes it zero. So no contribution comes from the end points.

4. The state vector of a particle of mass m in a deep square well potential, extended from $x = 0$ to L, at $t = 0$, is $|\psi(0)\rangle = \frac{1}{\sqrt{5}}\left(|\phi_1\rangle + 2|\phi_2\rangle\right)$ where $|\phi_1\rangle$ and $|\phi_2\rangle$ are the state vectors for the ground state and the first exited states. What will be the wave function at time $t = \frac{2mL^2}{\pi\hbar}$? Sketch the wave function at $t = 0$ and at $t = \frac{2mL^2}{\pi\hbar}$.

Solution: The state at time t is given by,

$$\psi(t) = \frac{1}{\sqrt{5}}\left[|\phi_1\rangle e^{-\frac{i}{\hbar}E_1 t} + 2|\phi_2\rangle e^{-\frac{i}{\hbar}E_2 t}\right].$$

Now, $-\frac{i}{\hbar}E_1 t = -\frac{i}{\hbar}\frac{\pi^2\hbar^2}{2mL^2}\times\frac{2mL^2}{\pi\hbar} = -i\pi$.

So, $e^{-\frac{i}{\hbar}E_1 t} = e^{-i\pi} = \cos\pi - i\sin\pi = -1$.

Similarly, $-\frac{i}{\hbar}E_2 t = -\frac{i}{\hbar}\frac{4\pi^2\hbar^2}{2mL^2}\times\frac{2mL^2}{\pi\hbar} = -4i\pi$.

So, $e^{-\frac{i}{\hbar}E_2 t} = e^{-4i\pi} = \cos 4\pi - i\sin 4\pi = 1$.

Thus, $\psi(t) = \frac{1}{\sqrt{5}}\left[2|\phi_2\rangle - |\phi_1\rangle\right]$.

Figure 12.W1 shows the sketches of the wave function at time 0 and $2mL^2/(\pi\hbar)$.

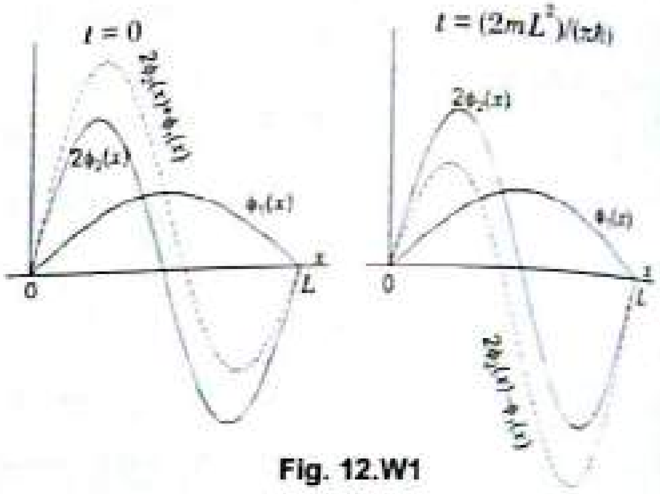


Fig. 12.W1

5. The wave function of a particle in a one-dimensional box, extended from $x = 0$ to L, is given as

$$\psi(x) = \sqrt{\frac{12}{L^3}}\,x \qquad \text{for } 0 < x \le L/2 - \epsilon$$

$$= \sqrt{\frac{12}{L^3}}(L - x) \qquad \text{for } L/2 + \epsilon < x < L$$

$$= 0 \qquad \text{for } x < 0 \text{ and } x > L.$$

In the range $\frac{L}{2} - \epsilon$ to $\frac{L}{2} + \epsilon$, the function $\psi(x)$ is such that it joins smoothly the two branches as shown in the Figure. Take ϵ to be infinitesimally small.

(a) Check that the wave function vanishes at $x = 0$ and L.

(b) Check that the wave function is normalized.

(c) Find the probability of finding the particle in ground state if an energy measurement is made.

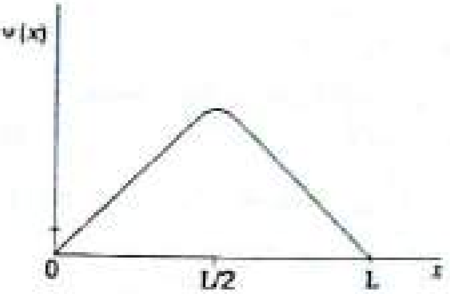


Fig. 12.W2

***Solution*:** **(a)** Put $x = 0$ and L in the given wave function and you get $\psi = 0$.

(b)

$$\int_{-\infty}^{\infty}|\psi(x)|^2\,dx = \int_0^{\frac{L}{2}-\epsilon}\frac{12}{L^3}x^2dx + \int_{\frac{L}{2}+\epsilon}^{L}\frac{12}{L^3}(L-x)^2dx + \int_{\frac{L}{2}-\epsilon}^{\frac{L}{2}+\epsilon}|\psi(x)|^2\,dx$$

In the limit $\epsilon \to 0$, this is,

$$= \frac{1}{2} + \frac{1}{2} + 0 = 1.$$

(c) The probability of finding the particle in the ground state is the same as that of getting the energy E_1. And this is equal to $|\langle\phi_1|\psi\rangle|^2$, where $\phi_1(x)$ is the energy eigenfunction corresponding to the ground state.

$$\langle\phi_1|\psi\rangle = \int_{-\infty}^{\infty}\phi_1^*(x)\psi(x)dx$$

$$= \int_0^{\frac{L}{2}-\epsilon} \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}\sqrt{\frac{12}{L^3}}\,x\,dx + \int_{\frac{L}{2}+\epsilon}^{L} \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}\sqrt{\frac{12}{L^3}}(L-x)\,dx = \sqrt{96}/\pi^2 .$$

Once again I have neglected the contribution from the range $\frac{L}{2}-\epsilon$ to $\frac{L}{2}+\epsilon$.

Thus the required probability is $|\langle\phi|\psi\rangle|^2 = 96/\pi^4$.

Think, why did I menotion the wave function separately for the range $\frac{L}{2}-\epsilon$ to $\frac{L}{2}+\epsilon$?

6. The wave function of a particle in a deep square well potential extending from $x = 0$ to $x = L$ is $\psi(x) = \sqrt{30}\,x(x-L)/L^i$ (a) Find the value of i. (b) Check that the wave function is normalized. (c) Find the average value of x in this state.

Solution: (a) Any wave function of a particle in one dimension has the dimensions of $1/\sqrt{L}$. Thus $i = 5/2$.

(b) $$\langle\psi|\psi\rangle = \int_{-\infty}^{\infty} \psi^*(x)\,\psi(x)\,dx = \frac{30}{L^5}\int_0^L x^2(x-L)^2\,dx = 1 .$$

(c) $$\langle x\rangle = \int_{-\infty}^{\infty} \psi^*(x)\,x\,\psi(x)\,dx = \frac{30}{L^5}\int_0^L x^3(x-L)^2\,dx = L/2.$$

7. A particle of mass m is subjected to a deep square well potential $V(x) = 0$ for $-L < x < L$ and $V(x) = \infty$ otherwise. Write the energy eigenvalues and eigenfunctions.

Solution: The energy eigenvalues are

$$E_n = \frac{n^2\pi^2\hbar^2}{(2L)^2},\ n = 1, 2, 3, \ldots..$$

To get the corresponding eigenfunctions, let me change the variable to $y = \frac{1}{2}(x+L)$. The range $-L < x < L$ is the same as $0 < y < L$. In terms of y, the potential is $V(y) = 0$ for $0 < y < L$ and $V(y) = \infty$ otherwise. The eigenfunction corresponding to the energy E_n is

$$\phi_n(y) = A_n \sin\frac{n\pi y}{L} .$$

In terms of x, $\phi_n(x) = A_n \sin\frac{n\pi(x+L)}{2L} = A_n \sin\left(\frac{n\pi x}{2L} + \frac{n\pi}{2}\right)$. For even value of n, $\phi_n(x) = A_n \sin\frac{n\pi x}{2L}$ or $-A_n \sin\frac{n\pi x}{L}$.

For odd values of n, $\phi_n(x) = A_n \cos\frac{n\pi x}{2L}$ or $-A_n \cos\frac{n\pi x}{2L}$.

Plus or minus sign does not change the state. The normalization constant A_n can be chosen as $\sqrt{\frac{2}{2L}} = \sqrt{\frac{1}{L}}$.

Thus $\phi_n(x) = \sqrt{\frac{1}{L}}\cos\frac{n\pi x}{2L}$ for $n = 1, 3, 5, \ldots..$

and $\phi_n(x)=\sqrt{\frac{1}{L}}\sin\frac{n\pi x}{L}$ for $n=2,4,6,\ldots$

8. A particle is in the ground state of a deep square well in the range $0<x<L$. Suddenly the wall $x=L$ of the well is shifted to $x=2L$, so as to make it a deep square well in the range $0<x<2L$. Immediately after this, the energy of the particle is measured. What will be the probability of getting the energy as the new ground state energy.

Solution: The wave function just before the shifting of the wall is

$$\psi(x)=\sqrt{\frac{2}{L}}\sin\frac{\pi x}{L} \text{ for } 0<x<L$$

$$=0 \text{ otherwise.}$$

This is the energy eigenfunction corresponding to the ground state in the original well. When the wall is shifted, the new ground state wave function becomes,

$$\phi(x)=\sqrt{\frac{2}{2L}}\sin\frac{\pi x}{2L} \text{ for } 0<x<2L$$

$$=0 \text{ otherwise.}$$

The actual wave function $\psi(x)$ is thus no more an eigenfunction of the Hamiltanian. The probability of getting the ground state energy in measurement is $|\langle\phi|\psi\rangle|^2$.

$$\langle\phi|\psi\rangle=\int_{-\infty}^{\infty}\phi^*(x)\psi(x)\,dx=\int_0^L\sqrt{\frac{2}{2L}}\sin\frac{\pi x}{2L}\sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}\,dx$$

$$=\frac{1}{L\sqrt{2}}\int_0^L\left(\cos\frac{\pi x}{2L}-\cos\frac{3\pi x}{2L}\right)dx$$

$$=\frac{1}{L\sqrt{2}}\left[\frac{\sin\frac{\pi x}{2L}}{\frac{\pi}{2L}}-\frac{\sin\frac{3\pi x}{2L}}{\frac{3\pi}{2L}}\right]_0^L$$

$$=\frac{8}{3\sqrt{2}\pi}$$

Thus the probability is $|\langle\phi|\psi\rangle|^2=\frac{32}{9\pi^2}$.

9. Consider a particle of mass 10^{-30} kg trapped in an infinitely deep potential well of width 0.5 nm. (a) Find the value of the wave number k in the ground state. (b) How many states are there having value of k between 10 nm^{-1} and 100 nm^{-1} (c) What is the density of states at $E=3\text{eV}$?

Solution: **(a)** $k=\frac{n\pi}{L}$. In ground state,

$$k=\frac{\pi}{L}=\frac{3.14}{0.5\,\text{nm}}=6.28\,\text{nm}^{-1}.$$

(b) For every interval π/L of k, there is one quantum state. The total k-interval is,

$$\Delta k=100\,\text{nm}^{-1}-10\,\text{nm}^{-1}=90\,\text{nm}^{-1}.$$

So, the number of states with k value in the given interval is,

$$\frac{90\,\text{nm}^{-1}}{6.28\,\text{nm}^{-1}} = 14.33\,.$$

There are 14 states in the given interval.

(c) Density of states is $\sqrt{\frac{m}{2\hbar^2\pi^2}}\,E^{-1/2}$. At $E = 3\text{eV}$, it is

$$\frac{10^{-15}}{10^{-34} \times 3.14 \times \sqrt{2}} \times \frac{1}{\sqrt{3 \times 1.6 \times 10^{-19}}} \quad \text{J}^{-1}\text{m}^{-1}$$

$$= \frac{1}{3.14 \times \sqrt{2} \times 10^{-19}} \times \frac{1}{\sqrt{3 \times 1.6 \times 10^{-19}}}$$

$$= 0.5\text{eV}^{-1}\,\text{nm}^{-1}\,.$$

The density of state is less than 1 in these units. With 0.5 nm wide well, the ground state energy will be about 0.3 eV. Thus 3 eV corresponds to around $n = 3$. Here, the separation between consecutive energy levels in more than an eV.

EXERCISES

1. An electron is contained in a one-dimensional box of width 2 Å. Calculate its minimum possible energy.

   Ans. 0.94 eV

2. A ball of mass 100 g is kept in a box of diameter 20 cm. Estimate the lower limit on its energy put by the quantum mechanical nature of the world.

   Ans. = 10^{-65}J

3. Let $|\phi_1\rangle$ and $|\phi_2\rangle$ be the ground state and the first excited state wave functions for a particle in a deep potential well of width L. Calculate $\langle x^2 \rangle$ for the state $\psi(x) = \frac{1}{\sqrt{5}}\left[|\phi_1\rangle - 2|\phi_2\rangle\right]$.

   Ans. $\frac{L^2}{3}\left(1 + \frac{11}{3\pi^2}\right)$

4. Let $|\phi_1\rangle$ and $|\phi_2\rangle$ be the ground state and the first excited state wave functions for a particle in a deep potential well of width L. The wave function of the particle at a particular time is $\psi(x) = \frac{1}{\sqrt{2}}\left[|\phi_1\rangle + |\phi_2\rangle\right]$. Calculate the uncertainty in the momentum.

   Ans. $\sqrt{\frac{5}{2}}\frac{\pi\hbar}{L}$

5. Prove that $\langle \phi_m | \text{P}_x^r | \phi_n \rangle = 0$ if r is an odd integer, $m + n$ is even and $|\phi_m\rangle$, $|\phi_n\rangle$ are stationary state wave functions of a particle in a deep square well potential.

6. With the same meaning of $|\phi_m\rangle$, $|\phi_n\rangle$ as in the previous problem, show that $\langle \phi_m | \text{P}_x^r | \phi_n \rangle = 0$ if $m \neq n$ and r is an even integer.

7. Prove that $\langle \phi_n | \text{P}_x^{2m} | \phi_n \rangle = \left(\frac{n\pi\hbar}{L}\right)^{2m}$ where m is an integer and $|\phi_n\rangle$ is an energy eigenfunction of a particle in a one-dimensional box of length L.

8. A particle of mass m is in an infinite square well potential $V(x)=0$ for $0<x<L$ and 0 otherwise. At time $t=0$, its wave function is $\psi(x)=\sqrt{\frac{2}{L}}\left(e^{\frac{3\pi ix}{L}}-e^{\frac{-3\pi ix}{L}}\right)$. What will be its wave function at time $t=\frac{mL^2}{2\pi\hbar}$?

Ans. $\frac{1-i}{\sqrt{L}}\left(e^{\frac{3\pi ix}{L}}-e^{\frac{-3\pi ix}{L}}\right)$

9. A particle of mass m is in a one-dimensional box of length L. Its wave function at time $t=0$ is a superposition of the ground state $|\phi_1\rangle$ and the first excited state $|\phi_2\rangle$, and is written as $\psi(x)=\frac{1}{\sqrt{2}}\left[|\phi_1\rangle-|\phi_2\rangle\right]$. Find the expectation value of x at time $t=\frac{2mL^2}{\pi\hbar}$.

Ans. $L\left(\frac{1}{2}-\frac{16L}{9\pi^2}\right)$

10. A particle in a deep square well potential extending from $x=0$ to $x=L$ has a wave function $\psi(x)=\sqrt{30}\,x(x-L)/L^{5/2}$.

(a) Sketch the wave function showing the labels clearly.

(b) What is the probability that the energy of the particle is found to be $\hbar^2\pi^2/\left(2mL^2\right)$?

Ans. (b) $960/\pi^4$, very close to 1

11. Calculate the momentum distribution function $a(p)$ for the ground state wavefunction of a particle in deep square well, extended from $x=0$ to $x=L$. Also find $|a(p)|^2$.

Ans. $\sqrt{\frac{\pi}{\hbar L^3}}\frac{1+e^{-\frac{ipL}{\hbar}}}{\left[\left(\frac{\pi}{L}\right)^2-\left(\frac{p}{\hbar}\right)^2\right]}$, $\frac{4\pi}{\hbar L^3}\frac{\sin^2\frac{pL}{2\hbar}}{\left[\left(\frac{p}{\hbar}\right)^2-\left(\frac{\pi}{L}\right)^2\right]^2}$

12. A particle is moving in an infinitely deep one-dimensional potential well $(0<x<L)$. At a certain time the particle is in the ground state of this potential and suddenly the wall at $x=L$ is shifted to $x=4L$. Calculate the probability of finding the particle in the first excited state.

Ans. $\frac{16}{9\pi^2}$

13. The state of a particle of mass m in a deep square well potential, extended from $x=0$ to $x=L$, is given by $|\psi(0)\rangle=\frac{1}{\sqrt{2}}\left[|\phi_1\rangle+|\phi_2\rangle\right]$ at time $t=0$. (a) Show that $|\psi(0)\rangle$ is normalized. (b) What is the value of the wave function $\psi(t)$ at $x=\frac{L}{4}$ at time $t=0$? (c) What is the value of $\psi(t)$ at $x=\frac{L}{4}$ at time $t=\frac{2mL^2}{\pi\hbar}$? (d) Find the values of x for which the value of the wave function is the same at $t=0$ and $t=\frac{2mL^2}{\pi\hbar}$.

Ans. (b) $\frac{1}{\sqrt{L}}\left(1+\frac{1}{\sqrt{2}}\right)$ (c) $\frac{1}{\sqrt{L}}\left(1-\frac{1}{\sqrt{2}}\right)$ (d) 0, L

14. Consider a particle of mass 10^{-27} kg confined in a one-dimensional box of width 10 cm (you can think of a one-dimensional model of an atom of hydrogen gas sample in a small container). (a) Find the ground state energy. (b) Find the number of states having energy less than 1.0 eV. (c) Find the density of states at 1.0 eV in unit of $\text{eV}^{-1}\text{mm}^{-1}$.

Ans. (a) $3\times10^{-20}\,\text{eV}$ (b) $\approx 5.8\times10^{9}$ (c) $1.8\times10^{56}\,\text{eV}^{-1}\text{mm}^{-1}$

POSTSCRIPT

A particle in a 2-D box

Let me imagine a world which is 2-dimentional and can be described by the Cartesian coordinates x and y. The particle's position is denoted by x, y and its linear momentum by p_x, p_y. The operator corresponding to x is multiplication by x, corresponding to y is multiplication by y, corresponding to p_x is $-i\hbar\frac{\partial}{\partial x}$ and corresponding to p_y is $-i\hbar\frac{\partial}{\partial y}$. The wave function is written as $\psi(x, y)$ which is function of both the variables x and y. Partial differentiations are used because the functions to be considered contain two variables x and y. While differentiating with respect to x, treat y as a constant and while differentiating with respect the y, treat x as a constant.

The kinetic energy operator is

$$K = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right].$$

P12.1 Hamiltonian for a particle in 2-D square box.

Consider a particle of mass m restricted to remain inside a square region $0 < x < L, 0 < y < L$. If the particle is inside this square, it is free to move and the potential is zero. But if it tries to move out from any of the four sides, it is pushed back into the square. The potential outside the square is ∞. So,

$$V(x,y) = 0 \quad \text{if } 0 < x < L \text{ and } 0 < y < L$$
$$= \infty \quad \text{otherwise}.$$

You can write $V(x,y) = V(x) + V(y)$

where, $V(x) = 0$ if $0 < x < L$

$= \infty$ otherwise

and $V(y) = 0$ if $0 < y < L$

$= \infty$ otherwise.

The Hamiltonian of the particle is given by

$$\text{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + V(x) + V(y)$$

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

$$= \text{H}_1 + \text{H}_2$$

where $H_1 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$ and $H_2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + V(y)$.

P12.2 The energy eigenvalues and eigenfunctions

The energy eigenfunctions for this system are given by

$$\phi_{n_1,n_2}(x,y) = \phi_{n_1}(x)\,\phi_{n_2}(y)$$

where $\phi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$ and $\phi_n(y) = \sqrt{\frac{2}{L}}\sin\frac{n\pi y}{L}$, and n_1, n_2 are positive integers.

The corresponding energy eigenvalues are given by

$$E_{n_1,n_2} = E_{n_1} + E_{n_2}$$

where $$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}.$$

So, $$\phi_{n_1,n_2}(x,y) = \frac{2}{L}\sin\frac{n_1\pi x}{L}\sin\frac{n_2\pi y}{L} \qquad \text{(P12.1)}$$

and $$E_{n_1,n_2} = \frac{\hbar^2\pi^2}{2mL^2}(n_1^2 + n_2^2). \qquad \text{(P12.2)}$$

I have stated the expressions for energy eigenvalues and eigenfunctions without solving the eigenvalue equation. You can check that these are indeed the correct solutions by putting these expressions in the eigenvalue equation. Let me do this.

$$\begin{aligned} \mathrm{H}\,\phi_{n_1,n_2}(x,y) &= [\mathrm{H}_1 + \mathrm{H}_2]\left[\phi_{n_1}(x)\,\phi_{n_2}(y)\right] \\ &= \mathrm{H}_1\left[\phi_{n_1}(x)\phi_{n_2}(y)\right] + \mathrm{H}_2\left[\phi_{n_1}(x)\phi_{n_2}(y)\right]. \qquad \text{(i)} \end{aligned}$$

Now $\mathrm{H}_1 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$. It has no dependence on y. For differentiating with respect to x, any y-dependent part of the function is to be treated as constant. So,

$$\begin{aligned} \mathrm{H}_1\left[\phi_{n_1}(x)\,\phi_{n_2}(y)\right] &= \left[\mathrm{H}_1\,\phi_{n_1}(x)\right]\,\phi_{n_2}(y) \\ &= \left[E_{n_1}\phi_{n_1}(x)\right]\,\phi_{n_2}(y) \\ &= E_{n_1}\phi_{n_1}(x)\,\phi_{n_2}(y). \end{aligned}$$

Similarly, $$\begin{aligned} \mathrm{H}_2\left[\phi_{n_1}(x)\,\phi_{n_2}(y)\right] &= \phi_{n_1}(x)\left[\mathrm{H}_2\,\phi_{n_2}(y)\right] \\ &= \phi_{n_1}(x)\left[E_{n_2}\phi_{n_2}(y)\right] \\ &= E_{n_2}\phi_{n_1}(x)\phi_{n_2}(y). \end{aligned}$$

So (i) becomes,

$$\begin{aligned} \mathrm{H}\phi_{n_1,n_2}(x,y) &= E_{n_1}\phi_{n_1}(x)\,\phi_{n_2}(y) + E_{n_2}\phi_{n_1}(x)\,\phi_{n_2}(y) \\ &= (E_{n_1} + E_{n_2})\phi_{n_1,n_2}(x,y). \end{aligned}$$

This proves my statements.

Note that these eigenvalues are not all nondegenerate. The eigenfunctions ϕ_{n_1,n_2} and ϕ_{n_2,n_1} are different if $n_1 \neq n_2$, but the energy eigenvalue is the same for the two. Apart from this, you may have cases where $n_1^2 + n_2^2 = n_3^2 + n_4^2$ for totally different pairs of integers.

P12.3 Energy eigenstates in the k-space

The energy eigenfunctions for a particle in a 2-D square box are

$$\phi_{n_1,n_2}(x,y)=\frac{2}{L}\sin\frac{n_1\pi x}{L}\sin\frac{n_2\pi y}{L}.$$

You can write this as $\phi_{n_1,n_2}(x,y)=\frac{2}{L}\sin k_x x\sin k_y y$.

The allowed values of k_x and k_y are

$$k_x=\frac{n_1\pi}{L} \text{ and } k_y=\frac{n_2\pi}{L} \qquad \text{(P12.3)}$$

where n_1 and n_2 are positive integers. In Figure P12.1, I have drawn k_x on one axis and k_y on the other. The dots at the points of intersection correspond to k_x, k_y values allowed by equation P12.3. Each dot thus corresponds to one energy eigenstate.

So the energy eigenstates (in fact, the representative dots) are distributed uniformly in the k-space (only positive values). You can see that there are four dots at the four corners of any given small square and each dot is shared by four small squares. So on the average, you have one dot per small square. Each small square has an area $(\pi/L)^2$ and thus, on the average, each area of $(\pi/L)^2$ in the k-space corresponds to one energy eigenstate.

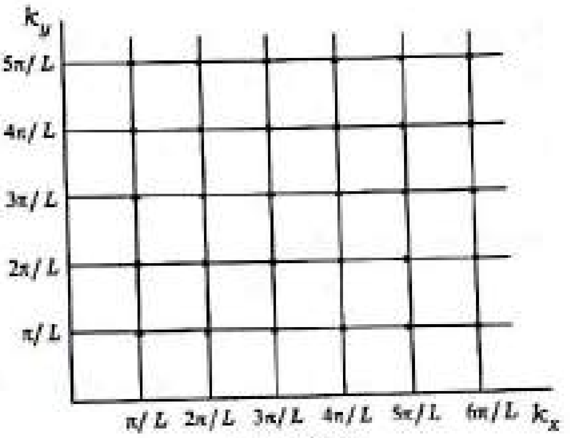


Fig. P12.1

P12.4 Density of states

To count the number of quantum states in the energy interval E to $E+dE$, I should find the area in k-space corresponding to this energy interval. Once that is done the remaining task is simple, just divide by $(\pi/L)^2$.

The dots in Figure P12.1 that correspond to a given energy E will satisfy

$$E=\frac{\hbar^2\pi^2}{2mL^2}(n_1^2+n_2^2)=\frac{\hbar^2}{2m}(k_x^2+k_y^2)$$

or, $$k_x^2+k_y^2=\frac{2mE}{\hbar^2}.$$

This is a circle of radius $k=\sqrt{\frac{2mE}{\hbar^2}}$ (see Figure P12.2). Similarly the dots that corresponds to the energy $E+dE$ will lie on a circle of radius $k+dk$.

The dots that correspond to the energy interval E to $E+dE$ will lie in the area enclosed between these two circles, one of radius k and the other of radius $k+dk$. This area is $\frac{1}{4}(2\pi k\,dk)$. The factor of $\frac{1}{4}$ appears

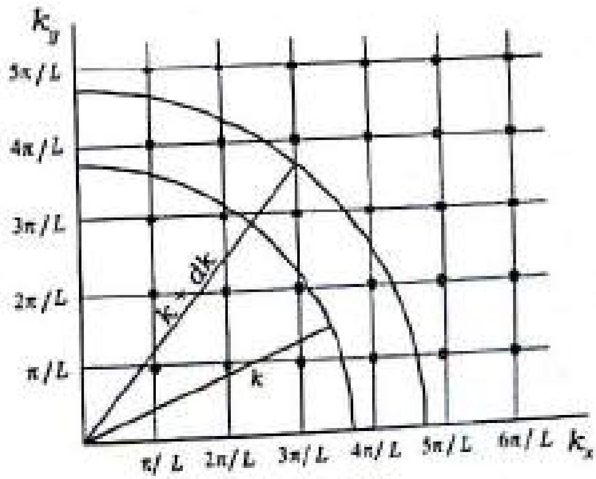


Fig. P12.2

because only the positive values of k_x, k_y are to be used.

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

$$dE = \frac{\hbar^2}{2m}(2k\,dk)$$

or
$$2\pi k\,dk = \frac{2m\pi}{\hbar^2}dE\,.$$

Thus the area in the k-space corresponding to the energy interval E to $E + dE$ is

$$\frac{1}{4}(2\pi k\,dk) = \frac{1}{4}\left(\frac{2m\pi}{\hbar^2}dE\right) = \frac{m\pi}{2\hbar^2}dE\,.$$

As each area of $(\pi/L)^2$ corresponds to one energy eigenstate, the number of states in the energy interval E to $E + dE$ is

$$dN = \frac{\frac{m\pi}{2\hbar^2}dE}{(\pi/L)^2} = \frac{m}{2\hbar^2\pi}L^2 dE\,.$$

The density of state is

$$\frac{dN}{dE} = \frac{m}{2\hbar^2\pi}L^2.$$

L^2 is the area of the square region in which the particle is confined. The density of states per unit area of the square is therefore,

$$\frac{1}{L^2}\frac{dN}{dE} = \frac{m}{2\hbar^2\pi}.$$

Note that the density of states is independent of energy.

In the case of 1-D box, the density of states is proportional to $E^{-1/2}$ (decreases with increase in energy). For 2-D box it is independent of E. I will calculate the DOS in the case of 3-D box in a later chapter and you will see that it is proportional to $E^{1/2}$ (increases with increase in energy).

13

Even Finite Well Will Do — Finite Square Well Potential

An infinitely deep square well potential keeps the particle bound for any energy that the particle can have. A finite square well potential has a similar shape, but the depth of the well is finite. I have shown such a potential well in Figure 13.1. The potential is zero in the region $-L/2 < x < L/2$ and V_0 outside it. I have purposely taken the range as $-L/2 < x < L/2$ because it makes the potential function $V(x)$ an even function. You remember, a function is called even if its values at x and $-x$ are the same. I will show that if the potential function is even, the Hamiltonian commutes with the parity operator and this makes the solutions of time independent Schrödinger equation somewhat simpler.

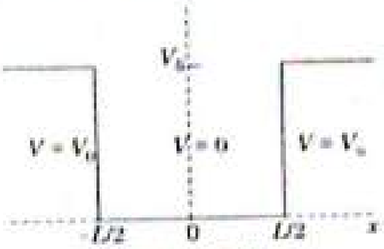


Fig. 13.1

13.1 Hamiltonian commutes with parity if $V(x)$ is even

The parity operator Π is defined by its action on a function, it replaces each x in the given function by $-x$. You have learnt in Chapter 8 that all even functions are eigenfunctions of Π with eigenvalue +1 and all odd functions are eigenfunctions of Π with eigenvalue -1. Here I will show that $[\Pi, H] = 0$ if $V(x)$ is an even function.

For any function $\psi(x)$,

$$\Pi\, H\psi(x) = \Pi\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x)$$

$$= \Pi\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right]$$

$$= -\frac{\hbar^2}{2m}\frac{d^2\psi(-x)}{dx^2} + V(-x)\psi(-x). \qquad \text{(i)}$$

Check that taking the double derivative with respect to x and $-x$ are the same.

Also,

$$H\,\Pi\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\Pi\psi(x)$$

$$= \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(-x)$$

$$= -\frac{\hbar^2}{2m}\frac{d^2\psi(-x)}{dx^2} + V(x)\psi(-x). \qquad \text{(ii)}$$

If the potential $V(x)$ is an even function of x, the expressions (i) and (ii) are equal. Hence $\Pi\, H\psi(x) = H\,\Pi\psi(x)$ for all $\psi(x)$, giving $\Pi H = H\Pi$. Thus, $[\Pi, H] = 0$

As Π and H commute, they should have a complete set of common eigenfunctions. This means, we can look for only those eigenfunctions of H which are also eigenfunctions of Π, that is, which are either odd or even functions. Any other eigenfunction of H has to be a linear combination of these. If an eigenvalue of H is nondegenerate it has to be either even or odd. If an eigenvalue is degenerate, we can choose even or odd independent eigenfunctions to form a complete set.

13.2 Eigenvalues and eigenfunctions of energy for a finite square well potential

The potential function $V(x)$ for a finite square well potential may be written as,

$$V(x) = 0 \quad \text{for} \quad -L/2 < x < L/2$$
$$= V_0 \quad \text{otherwise.}$$

The depth of the well is V_0 and its width is L. For a bound state, the total energy E is less than V_0. The potential is an even function of x and hence I look only for the eigenfunctions of definite parity.

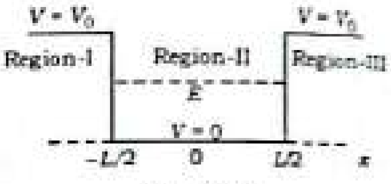


Fig. 13.2

The potential changes discontinuously at $x = -L/2$ and $L/2$. Thus the differential equation in the Schrödinger equation (time independent) must be solved separately in the three regions shown in Figure 13.2. In Region-I, the potential is V_0. So the equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\phi_I(x)}{dx^2} + V_0\,\phi_I(x) = E\,\phi_I(x)$$

or
$$\frac{d^2\phi_I(x)}{dx^2} - \frac{2m}{\hbar^2}(V_0 - E)\,\phi_I(x) = 0$$

or
$$\frac{d^2\phi_I(x)}{dx^2} - \gamma^2\phi_I(x) = 0$$

where
$$\gamma = +\sqrt{\frac{2m}{\hbar^2}(V_0 - E)}. \tag{13.1}$$

I am interested in the bound states, so $E < V_0$ and hence γ is a real, positive quantity. The solution of the above differential equation is,

$$\phi_I(x) = Ae^{\gamma x} + Be^{-\gamma x}.$$

One boundary condition on a wave function is that it must remain finite at all points. Region I contains large negative values of x and hence the constant B in the above expression must be zero. Thus,

$$\phi_I(x) = Ae^{\gamma x} \quad \text{for} \quad x < -L/2. \tag{i}$$

In Region-II, the potential $V(x)$ is zero so that the Schrödinger equation is

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

or
$$\frac{d^2\phi_{II}(x)}{dx^2} + \frac{2mE}{\hbar^2}\phi_{II}(x) = 0$$

or
$$\frac{d^2\phi_{II}(x)}{dx^2} + k^2\phi_{II}(x) = 0$$

where
$$k = +\sqrt{\frac{2mE}{\hbar^2}}. \tag{13.2}$$

Check that E is positive and so k is a real, positive quantity. The solution of this equation may be written as,

$$\phi_{II}(x) = C\sin kx + D\cos kx \quad \text{for} \quad -L/2 < x < L/2. \tag{ii}$$

The Schrödinger equation in Region-III has the same form as that in Region-I. The solution is

$$\phi_{III}(x) = Ee^{\gamma x} + Fe^{-\gamma x}.$$

As Region-III contains large positive values of x and the wave function must be finite everywhere, the constant E must be zero. Thus

$$\phi_{III}(x) = Fe^{-\gamma x} \quad \text{for} \quad x > L/2 . \tag{iii}$$

The use of the symbols k and γ is almost standard. They are defined in a way to make them real, positive numbers. The symbol γ is used when the total energy is less than the potential energy and k when the total energy is larger than the potential energy. The quantity $V_0 - E$ appearing in the expression of γ is the difference of the total energy from the top of the potential. In other words, it tells how much less the total energy is from the potential energy. The wave function has exponentially decaying form in this case. The quantity E appearing in the expression of k is the difference of the energy from the bottom of the potential. In other words, it tells how much more is the total energy from the potential energy. The wave function has oscillatory form in this case.

Even eigenfunctions

Let us first search for the even eigenfunctions of the Hamiltonian. Inside the well, that is, in Region-II, we have a $\sin kx$ term and a $\cos kx$ term in the eigenfunction as given in (ii). The region itself contains positive and negative values of x. The term $\sin kx$ gives an odd function. If $\phi_{II}(x)$ is part of an even eigenfunction, the constant C should be zero. Thus for even eigenfunctions,

$$\phi_{II}(x) = D\cos kx . \tag{iv}$$

To make $\psi(-x) = \psi(x)$ for $|x| > L/2$ (See equations (i) and (iii)), we must have $A = F$. So, the even eigenfunctions must have the following form:

$$\begin{aligned} \phi_{I}(x) &= Ae^{\gamma x} && \text{for} \quad x < -L/2 \\ \phi_{II}(x) &= D\cos kx && \text{for} \ -L/2 < x < L/2 \\ \phi_{III}(x) &= Ae^{-\gamma x} && \text{for} \quad x > L/2. \end{aligned} \tag{13.3}$$

What are A and D and what are k and γ? The constants k and γ are related to the energy eigenvalue E. Can I take any value of E, construct γ and k from Equation 13.1 and 13.2 and get an eigenfunction from Equation 13.3? It is not so. The eigenfunctions must satisfy the boundary conditions that $\phi(x)$ and $\dfrac{d\phi(x)}{dx}$ are continuous everywhere. The continuity of $\phi(x)$ at $x = -L/2$ gives

$$\phi_{I}(x = -L/2) = \phi_{II}(x = -L/2)$$

or

$$Ae^{-\gamma L/2} = D\cos(kL/2) . \tag{v}$$

The continuity of $d\phi/dx$ at $x = -L/2$ gives

$$\left.\frac{d\phi_I}{dx}\right|_{x=-L/2} = \left.\frac{d\phi_{II}}{dx}\right|_{x=-L/2}$$

or

$$\gamma Ae^{-\gamma L/2} = kD\sin(kL/2) . \tag{vi}$$

Dividing (vi) by (v),

$$\gamma = k\tan\frac{kL}{2} \tag{vii}$$

or,

$$\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} = \sqrt{\frac{2mE}{\hbar^2}}\tan\left(\frac{L}{2}\sqrt{\frac{2mE}{\hbar^2}}\right). \tag{13.4}$$

This equation in E has some specific solutions and only these values of E are the energy eigenvalues. This equation can be solved using a computer and methods of numerical analysis. Here I give a simple graphical method to solve this equation.

Let me write $\eta = \frac{\gamma L}{2}$ and $\xi = \frac{kL}{2}$. Equation (vii) is then

$$\eta = \xi \tan \xi . \tag{viii}$$

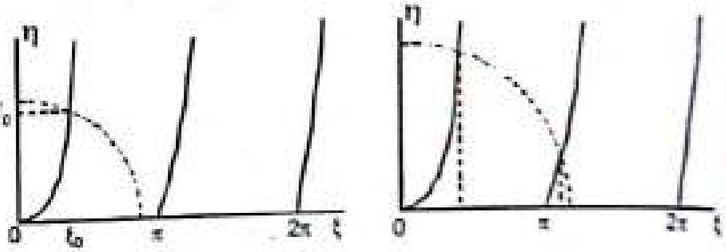
Also,

$$\eta^2 + \xi^2 = \frac{L^2}{4}\left(\gamma^2 + k^2\right) = \frac{L^2}{4}\left[\frac{2m(V_0 - E)}{\hbar^2} + \frac{2mE}{\hbar^2}\right]$$

$$= \frac{mV_0L^2}{2\hbar^2} \tag{ix}$$

which is a constant for a given particle and a given potential well. Both η and ξ are positive because I had chosen k, γ to be positive.

Plot η versus ξ using equation (viii) and also equation (ix), with the same axes and locate the points of intersection. The values of η, ξ corresponding to these points give the possible values of E. These plots are given in Figure 13.3. Look at the part (a) of the figure first. The solid curves represent the equation $\eta = \xi \tan \xi$. It has several branches. Remember, I am only showing the positive values of ξ and η. From $\xi = 0$ to $\pi/2$, $\tan \xi$ and hence η is positive (first branch). At $\xi = \pi/2$, the function discontinuously jumps from $+\infty$ to $-\infty$ and remains negative till $\xi = \pi$ where it becomes zero. From $\xi = \pi$ to $3\pi/2$ it remains positive (second branch) and so on.



(a) (b)

Fig. 13.3

The equation

$$\eta^2 + \xi^2 = \frac{mV_0L^2}{2\hbar^2} = R^2$$

is represented by the circular curve. If the radius R of this circle is less than π, it intersects only the first branch and there is only one point of intersection (ξ_0, η_0) as shown in Figure 13.3a.

Once η_0, ξ_0 are obtained, you can get $k = 2\xi_0/L$ or $\gamma = 2\eta_0/L$. From Equations 13.1 or 13.2 you then get the energy eigenvalue. Thus if

$$\left(\frac{mV_0L^2}{2\hbar^2}\right)^{1/2} < \pi$$

or

$$V_0L^2 < \frac{2\hbar^2\pi^2}{m}$$

there is only one bound state corresponding to even eigenfunctions.

If the potential is such that

$$\frac{2\hbar^2\pi^2}{m} < V_0L^2 < \frac{8\hbar^2\pi^2}{m}.$$

the radius of the circle represented by equation (ix) will be between π and 2π and the circle will cut two branches of the solid curves (Figure 13.3b). Thus there will be two values of energy. In this case, there are two bound states corresponding to the even eigenfunctions. Similarly if the radius of the circle is between 2π and 3π, there are three bound states corresponding to even eigenfunctions, and so on.

Once k, γ are obtained from the points of intersection, you can write the eigenfunction. Using equation (v),

$$D = A\frac{e^{-\gamma L/2}}{\cos(kL/2)}.$$

So that the eigenfunction is

$$\begin{aligned}\phi(x) &= Ae^{\gamma x} && \text{for} \quad x < -L/2 \\ &= A\frac{e^{-\gamma L/2}}{\cos(kL/2)}\cos kx && \text{for} \quad -L/2 < x < L/2 \\ &= Ae^{-\gamma x} && \text{for} \quad x > -L/2.\end{aligned} \tag{13.5}$$

The constant A can be obtained from the normalization condition

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

Odd eigenfunctions

Now let us search for the odd eigenfunctions. Look at equations (i), (ii) and (iii) again. Inside the well, we have both $\sin kx$ and $\cos kx$ terms. If it is a part of an odd function, $\cos kx$ term should be zero. Thus $D = 0$. Also for the regions I and III, that is, $|x| > L/2$, $\phi(x) = -\phi(-x)$. This gives $A = -F$. The odd eigenfunction must be of the form

$$\begin{aligned}\phi_I(x) &= Ae^{\gamma x} && \text{for} \quad x < -L/2 \\ \phi_{II}(x) &= C\sin kx && \text{for} \quad -L/2 < x < L/2 \\ \phi_{III}(x) &= -Ae^{-\gamma x} && \text{for} \quad x > L/2.\end{aligned} \tag{13.6}$$

Apply the continuity equation on ϕ and $\frac{d\phi}{dx}$ at $x = -L/2$. This gives,

$$Ae^{-\gamma L/2} = -C\sin(kL/2)$$

and $$A\gamma e^{-\gamma L/2} = Ck\cos(kL/2).$$

From these equations,

$$\gamma = -k\cot(kL/2)$$

or $$\frac{\gamma L}{2} = -\frac{kL}{2}\cot\left(\frac{kL}{2}\right)$$

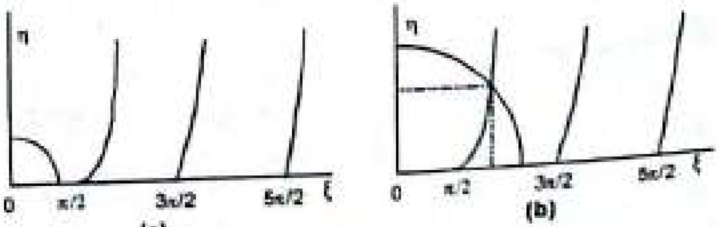
or $$\eta = -\xi\cot\xi$$

or, $$\eta = \xi\tan(\xi + \pi/2) \tag{x}$$

with the same definition of ξ and η as before. This equation is identical to that in (viii) except that ξ is replaced by $\xi + \pi/2$ in the argument of the tangent function. The solid lines in Figure 13.4 show this plot. Part (a) of this figure corresponds to the case when the radius of the circle

$$\eta^2 + \xi^2 = \frac{mV_0L^2}{2\hbar^2}$$

is less than $\pi/2$. The circle does not intersect any branch of the curve $\eta = \xi\tan(\xi + \pi/2)$ and hence there is no bound state corresponding to odd eigenfunctions. Part (b) of Figure 13.4 shows a case when the radius is larger than $\pi/2$ but less than $3\pi/2$. In this case there is one point of intersection and hence one bound state corresponding to an odd eigenfunction



(a) (b)

Fig. 13.4

appears. If the radius is between $3\pi/2$ and $5\pi/2$, the circle will intersect two branches of the solid curves giving two such bound states and so on. Once the energy eigenvalues are obtained from the points of intersection, the corresponding eigenfunctions are obtained in the same way as was done for even eigenfunctions. These are

$$\begin{aligned} \phi(x) &= Ae^{\gamma x} && \text{for} \quad x < -L/2 \\ &= -A\frac{e^{-\gamma L/2}}{\sin(\gamma L/2)}\sin kx && \text{for} \quad -L/2 < x < L/2 \\ &= -Ae^{-\gamma x} && \text{for} \quad x > L/2. \end{aligned} \tag{13.7}$$

In the table below I show the number of bound states for various ranges of V_0L^2. This quantity (V_0L^2) is also called the *strength* of the potential well. The shape of the eigenfunctions for some of the lowest energy eigenvalues are sketched in Figure 13.5.

R	V_0L^2	Even eigen-functions	Odd eigen-functions	No. of bound states
$<\pi/2$	$<\dfrac{\hbar^2\pi^2}{2m}$	1	0	1
$\pi/2$ to π	$\dfrac{\hbar^2\pi^2}{2m}$ to $\dfrac{4\pi^2\hbar^2}{2m}$	1	1	2
π to $3\pi/2$	$\dfrac{4\hbar^2\pi^2}{2m}$ to $\dfrac{9\pi^2\hbar^2}{2m}$	2	1	3
$3\pi/2$ to 2π	$\dfrac{9\hbar^2\pi^2}{2m}$ to $\dfrac{16\pi^2\hbar^2}{2m}$	2	2	4
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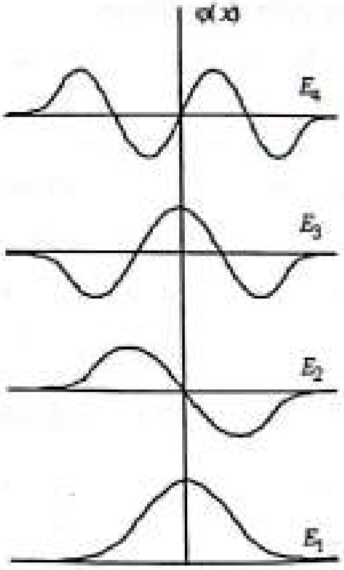

Fig. 13.5

13.3 Special features

The features shown by energy eigenvalues and eigenfunctions for a particle in a deep square well potential are also present qualitatively in case of finite square well potential. Thus we have a nonzero minimum energy, discrete energy eigenvalues, more nodal points (where $\phi = 0$) appearing in an eigenfunction corresponding to a higher energy, etc. However, there are two new features in the finite well potential.

(a) Finite number of bound states

Depending on the strength of the potential well (V_0L^2), we may have one, two or more number of bound states. There is at least one bound state corresponding to an even eigenfunction. Existence of other bound states depends on the strength of the potential. In contrast, you have infinite number of bound states in a deep potential well.

(b) Barrier penetration

Look at the wave function in Region-I or Region-III (Equations 13.6 and 13.7). Here $|x| > L/2$ and the potential energy $V(x)$ is larger than the total energy for any bound state. This is classically forbidden range as this corresponds to negative kinetic energy in classical mechanics. But the wave function in these regions is not zero. This means that there is a finite probability of finding the particle outside the well. This phenomenon of particle getting into classically forbidden regions is called *barrier* *penetration*. We had talked about it while discussing energy–time uncertainty. For a finite potential well, the wave function in the classically forbidden region decays exponentially with a length scale of $1/\gamma$. This means, the magnitude of the wave function becomes negligible as one goes few times of $1/\gamma$ into this region.

If we do find the particle in Region-I or Region-III, what is its kinetic energy? Is it negative as may appear from $E = K + V$? No, it is not. If you do locate the particle, the state of the particle is no more the same as it was before the measurement. The energy of the particle will also be different from the value corresponding to the bound state the particle had.

13.4 Physical situations

Finite square well potential is a favourite for theoretical physicists. Whenever they need an attractive force model, the first approximation that comes to mind is the square well potential. There are many situations in nature where square well potential can be taken as a good approximation. I will describe two of them.

(a) Free electrons in metal

Why are metals good conductor of electricity? The simplest answer is that metals have free electrons which are free to move anywhere in the whole body of the metal but cannot come out of it. The next level of information is added when we say that each metal has a work function Φ and if a free electron is given an energy equal to or greater than Φ, it may come out of the metal. This situation may be represented by a square well potential of depth Φ. When the electron is inside the metal, the potential is zero, (constant potential taken as zero). If the electron comes out its energy is increased by Φ.

Fig. 13.6

Can this situation be described by a finite square well potential? Yes and No. Yes, because under the assumptions made, the potential remains zero inside and Φ outside. And No, because it is not a 1-dimensional world. The potential described corresponds to 3-dimensional square well potential which has some different features.

(b) Deuteron problem

A deuteron is a nucleus containing a proton and a neutron. In other words it is the nucleus of a heavy hydrogen atom. The two particles, proton and neutron, are bound in a deuteron by nuclear forces. There is no Coulomb potential as neutron is uncharged. The attractive nuclear potential between the particles can be approximated by an equivalent square well potential written in terms of the separation r between the particles. For large values of r, the nuclear force is almost zero and you can take the potential to be zero. As such it is a three-dimensional problem, but we can represent it by an equivalent one-dimensional problem.

As the particles come within a distance of about a femtometer (10^{-15} m), attractive nuclear force starts operating, making the potential negative. As r cannot be negative, we represent it by a high potential wall at $r = 0$. Such an interaction between a proton and a neutron may be represented by a potential of the shape shown in Figure 13.7.

The problem is equivalent to that of a single particle of mass $\mu = 2m_p m_n/(m_p + m_n)$ moving in a potential $V(x)$ with the same shape as $V(r)$ shown here. As $m_p \approx m_n$, the value of $\mu \approx m_p/2$.

The binding energy of a deuteron is 2.2 MeV. It means, if 2.2 MeV energy is given to a deuteron nucleus, the proton and the neutron may separate from each other. If the energy is zero in this free state, that in the bound state is –2.2 MeV. The average separation between the proton and a neutron is about 2.0 fm. These are experimentally measured values. These values can be obtained theoretically if we

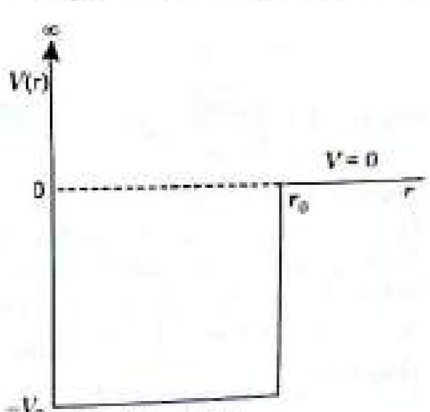

Fig. 13.7

represent the nuclear interaction by a potential of the shape shown in Figure 13.7 with $V_0 \approx 36$ MeV and $r_0 = 2.0$ fm. These values give an idea of the strength of nuclear interaction.

13.5 You learned in this chapter

- If the potential $V(x)$ is an even function, the parity operator commutes with the Hamiltonian. In such a case, energy eigenfunctions may be taken to have definite parity (even or odd).
- A finite square well potential allows a finite number of bound states, the minimum being one.
- The energy eigenfunction corresponding to the lowest energy is an even function. For higher energies odd and even eigenfunctions appear alternately.
- The wave function corresponding to a bound state in a finite square well potential penetrates into the classically forbidden regions.
- The wave function in the classically forbidden region decays exponentially whereas that in the allowed region has oscillatory nature.

Solved Problems

1. A particle of mass m moves in a potential given by

$$V(x) = \infty \quad \text{for} \quad x < 0$$
$$= 0 \quad \text{for} \quad 0 < x < L$$
$$= V_0 \quad \text{for} \quad x > L.$$

(a) Write the general form of the stationary state wave function in the three regions. (b) Applying the boundary conditions, find the transcendental equation satisfied by the energy eigenvalue E. (c) Check that the wave functions are the same as the odd solutions in the case of a symmetric potential well extended from $-L$ to $+L$.

Solution:

(a) The potential is sketched in Figure 13.W1. The general form of the energy eigenfunctions is

$$\phi(x) = 0 \quad \text{for} \quad x < 0$$
$$= A\sin kx + B\cos kx \quad \text{for} \quad 0 < x < L$$
$$= Ce^{-\gamma x} \quad \text{for} \quad x > L$$

where $k = \sqrt{\dfrac{2mE}{\hbar^2}}$ and $\gamma = \sqrt{\dfrac{2m(V_0 - E)}{\hbar^2}}$.

I wrote this directly. The logic is simple. $V = \infty$ in Region-I, so the eigenfunction is zero. Region-II has E > V, so I wrote oscillatory (sine and cosine) eigenfunction here. Region-III is classically forbidden so the eigenfunction must be exponentially decaying.

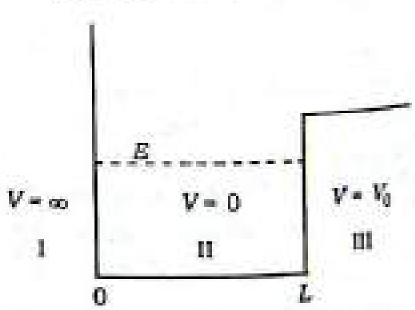

Fig. 13.W1

(b) Write the energy eigenfunctions in the three regions as ϕ_I, ϕ_{II}, ϕ_{III} and apply the boundary conditions.

$$\phi_I(0) = \phi_{II}(0) \quad \text{gives} \quad B = 0$$

and $$\phi_{II}(L) = \phi_{III}(L) \quad \text{gives}$$

$$A\sin kL = Ce^{-\gamma L}. \tag{i}$$

Also, $\left.\frac{d\phi_{II}}{dx}\right|_{x=L} = \left.\frac{d\phi_{III}}{dx}\right|_{x=L}$ gives

$$kA\cos kL = -\gamma Ce^{-\gamma L}. \tag{ii}$$

Dividing (ii) by (i),

$$k\cot kL = -\gamma$$

or
$$\sqrt{\frac{2mE}{\hbar^2}}\cot\left(\sqrt{\frac{2mE}{\hbar^2}}\,L\right) = -\sqrt{\frac{2m(V_0 - E)}{\hbar^2}}. \tag{iii}$$

This is the transcendental equation in energy.

(c) Equation (iii) is the same as that obtained for the odd eigenfunction of the symmetric well potential dealt in the chapter, except that $L/2$ is replaced by L. The eigenfunction in the present case can also be obtained from the odd eigenfunctions of the symmetric well with width $-L$ to $+L$. This is because the matching conditions at the boundary ($x = L$) will be the same in the two conditions and the other boundary condition that the wave function is zero at $x = 0$ in the given potential (because the potential goes to infinity) is also satisfied by the odd solutions of symmetric square well potential with width $-L$ to $+L$.

2 Show that the ground state energy of a particle of mass m in a finite square well potential of width L is less than that in infinite square well potential of the same width.

Solution: The ground state energy eigenvalue can be obtained from the intersection of the first branch of the curve $\eta = \xi\tan\xi$ and $\xi^2 + \eta^2 = R^2$ where the symbols have the same meaning as defined in the text. This point of intersection must correspond to a value of ξ less than $\pi/2$. This is because at $\xi = \pi/2$, the function $\eta = \xi\tan\xi$ goes to infinity and for $\xi > \pi/2$, the first branch does not exists. So for any finite potential V_0, $\xi < \pi/2$.

So
$$\frac{2mE}{\hbar^2}\frac{L^2}{4} < \frac{\pi^2}{4}$$

or
$$E < \frac{\pi^2\hbar^2}{2mL^2}.$$

This proves the result.

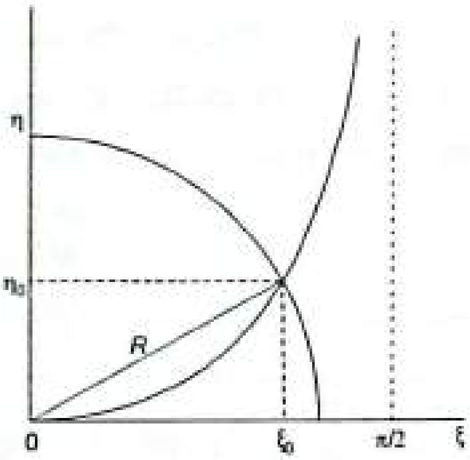

Fig. 13.W2

3 Consider a particle in a potential shown in Figure 13.W3. Find the transcendental equation in the energy eigenvalue E for bound states.

Solution: As is clear from the figure, the energy E should be negative for bound states. We can define four regions,

Region-I: $x < 0$, Region-II: $0 < x < L_1$, Region-III: $L_1 < x < L_2$ and Region-IV: $x > L_2$. The wave function for a bound state at energy E can be written as,

$$\phi_I(x) = 0$$
$$\phi_{II}(x) = Ae^{\gamma x} + Be^{-\gamma x}$$
$$\phi_{III}(x) = C\sin kx + D\cos kx$$
$$\phi_{IV}(x) = Fe^{-\gamma x}$$

where
$$\gamma = \sqrt{\frac{-2mE}{\hbar^2}} \text{ and } k = \sqrt{\frac{2m(V_0 + E)}{\hbar^2}}.$$

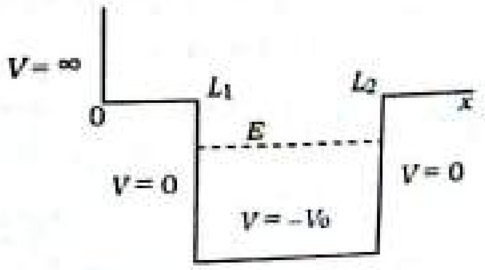

Fig. 13.W3

Note that the definitions of k and γ are the same as those given in text (Equations 13.1 and 13.2). The quantity $(-E)$ appearing in the expression of γ gives how much less is the total energy E from the potential energy in Region-II and Region-IV. The quantity $(V_0 + E)$ appearing in the expression of k gives how much more is the total energy E from the potential energy in Region-III.

Now apply the boundary conditions. First use continuity at $x = 0$.

$$\phi_I\big|_{x=0} = \phi_{II}\big|_{x=0}. \text{ This gives } B = -A.$$

So the wave function in Region II is,

$$\phi_{II}(x) = A(e^{\gamma x} - e^{-\gamma x}) = 2A\sinh(\gamma x).$$

Now use continuity at $x = L_1$.

$$\phi_{II}\big|_{x=L_1} = \phi_{III}\big|_{x=L_1}.$$

This gives, $\quad 2A\sinh(\gamma L_1) = C\sin kL_1 + D\cos kL_1$. (i)

Now match the slopes at $x = L_1$.

$$\left.\frac{d\phi_{II}}{dx}\right|_{x=L_1} = \left.\frac{d\phi_{III}}{dx}\right|_{x=L_1}.$$

This gives, $\quad 2A\gamma\cosh(\gamma L_1) = k(C\cos kL_1 - D\sin kL_1)$ (ii)

Apply continuity at $x = L_2$

$$\phi_{III}\big|_{x=L_2} = \phi_{IV}\big|_{x=L_2}.$$

This gives, $\quad C\sin kL_2 + D\cos(kL_2) = Fe^{-\gamma L_2}$. (iii)

And finally match the slopes at $x = L_2$

$$\left.\frac{d\phi_{III}}{dx}\right|_{x=L_2} = \left.\frac{d\phi_{IV}}{dx}\right|_{x=L_2}.$$

This gives, $\quad k(C\cos kL_2 - D\sin kL_2) = -\gamma Fe^{-\gamma L_2}$. (iv)

My strategy will be to eliminate A from (i) and (ii) to get a relation between C and D, and eliminate F from (iii) and (iv) to get another relation between C and D. When you demand consistency between these two relations you get an equation in energy. So multiply (i) by $\gamma\cosh(\gamma L_1)$, (ii) by $\sinh(\gamma L_1)$, and compare. You get,

$$C\gamma\cosh(\gamma L_1)\sin kL_1 + D\gamma\cosh(\gamma L_1)\cos kL_1 = Ck\sinh(\gamma L_1)\cos kL_1 - Dk\sinh(\gamma L_1)\sin kL_1$$

or $\quad C\left[\gamma\cosh(\gamma L_1)\sin kL_1 - k\sinh(\gamma L_1)\cos kL_1\right] = -D\left[\gamma\cosh(\gamma L_1)\cos kL_1 + k\sinh(\gamma L_1)\sin kL_1\right]$

giving $\quad \dfrac{C}{D} = \dfrac{\gamma\cosh(\gamma L_1)\cos kL_1 + k\sinh(kL_1)\sin kL_1}{k\sinh(\gamma L_1)\cos kL_1 - \gamma\cosh(kL_1)\sin kL_1}$. (v)

Now multiply (iii) by $-\gamma$ and compare with (iv),

$$-\gamma C\sin kL_2 - \gamma D\cos kL_2 = kC\cos kL_2 - kD\sin kL_2$$

or $\quad C(k\cos kL_2 + \gamma\sin kL_2) = D(k\sin kL_2 - \gamma\cos kL_2)$

giving $\quad \dfrac{C}{D} = \dfrac{k\sin kL_2 - \gamma\cos kL_2}{k\cos kL_2 + \gamma\sin kL_2}$. (vi)

From (v) and (vi),

$$\frac{\gamma\cosh(\gamma L_1)\cos kL_1 + k\sinh(\gamma L_1)\sin kL_1}{k\sinh(\gamma L_1)\cos kL_1 - \gamma\cosh(kL_1)\sin kL_1} = \frac{k\sin kL_2 - \gamma\cos kL_2}{k\cos kL_2 + \gamma\sin kL_2}$$

or $$\frac{\gamma + k\tanh(\gamma L_1)\tan(kL_1)}{k\tanh(\gamma L_1) - \gamma\tan(kL_1)} = \frac{k\tan(kL_2) - \gamma}{k + \gamma\tan(kL_2)}.$$

This is the required equation in energy. Remember when you write k and γ explicitly, the energy E is the only variable in this equation.

4. Consider a particle of mass m confined to a finite square well potential of length L. The particle is found to be in a bound state with energy $\frac{\hbar^2\pi^2}{8mL^2}$ above the bottom of the well. Find the depth of the potential well.

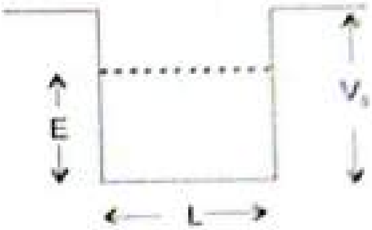

Fig. 13.W4

Solution:

$$k = \sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{2m}{\hbar^2}\cdot\frac{\hbar^2\pi^2}{8mL^2}} = \frac{\pi}{2L}.$$

$$\xi = k\frac{L}{2} = \frac{\pi}{2L}\cdot\frac{L}{2} = \frac{\pi}{4}.$$

Defining $\gamma = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$ and $\eta = \gamma\frac{L}{2}$, the boundary condition demands $\eta = \xi\tan\xi = \frac{\pi}{4}\tan\frac{\pi}{4} = \frac{\pi}{4}$.

But $$\xi^2 + \eta^2 = \left(\frac{L}{2}\right)^2 \times \frac{2mV_0}{\hbar^2}$$

so, $$\frac{\pi^2}{16} + \frac{\pi^2}{16} = \frac{mL^2V_0}{2\hbar^2}$$

or, $$V_0 = \frac{\pi^2\hbar^2}{4mL^2}.$$

5. A particle is in its first excited state in a finite square well potential extended from $x = -L/2$ to $x = L/2$. The maximum value of the wave function, at a particular instant, is $\psi = A$ and it occurs at $x = L/3$. Find the value of the function at $x = L/2$.

Solution: In the first excited state, the wave function is of the form $\psi = A\sin kx$. The maximum value of the wave function is A. According to the question, this occurs at $x = L/3$. This means,

Fig. 13.W5

$$A = A\sin\frac{kL}{3}$$

or, $$\frac{kL}{3} = \frac{\pi}{2} \text{ or } k = \frac{3\pi}{2L}.$$

The wave function at $x = L/2$ is

$$\psi = A\sin\frac{kL}{2} = A\sin\left(\frac{3\pi}{2L}\times\frac{L}{2}\right) = \frac{A}{\sqrt{2}}.$$

6. A finite square well potential has length L and depth V_0. A particle of mass $\frac{2\hbar^2}{V_0L^2}$ is trapped in this potential. Show that it has only one bound state and the energy corresponding to this state satisfies $\cos\left(\sqrt{E/V_0}\right) = \sqrt{E/V_0}$.

Solution: With standard notations,

$$\eta^2 + \xi^2 = \left(\frac{L}{2}\right)^2 \left[\frac{2mV_0}{\hbar^2}\right] = \frac{V_0 L^2}{2\hbar^2} \times \frac{2\hbar^2}{V_0 L^2} = 1$$

Thus, $\sqrt{\eta^2 + \xi^2} < \frac{\pi}{2}$ and hence only one bound state occurs. For the energy E,

$$\eta = \xi \tan \xi$$

or, $$\tan \xi = \frac{\eta}{\xi} = \frac{\sqrt{1-\xi^2}}{\xi}$$

or, $$\cos \xi = \xi$$

But $$\xi = \frac{L}{2} \times \sqrt{\frac{2mE}{\hbar^2}} = \frac{L}{2}\sqrt{\frac{2E}{\hbar^2} \times \frac{2\hbar^2}{V_0 L^2}} = \sqrt{\frac{E}{V_0}}.$$

Thus $$\cos\left(\sqrt{\frac{E}{V_0}}\right) = \sqrt{\frac{E}{V_0}}.$$

EXERCISES

1. Consider a deep square well potential of width L. Choose the origin at the middle of the well and write the energy eigenfunctions. Check that these have definite parity.
2. An electron is trapped by a finite square well potential of depth 10 eV and width 5 angstrom. How many bound states are possible? **Ans.** 3
3. An electron moves in a finite square well potential extended from $x = -L/2$ to $L/2$. The energy of the particle is 2 eV less than the top of the well. The wave function at the edge $x = L/2$ of the well is ψ_0. Find the length x_0 so that $\psi(L/2 + x_0) = \psi_0/e$. **Ans.** ≈1.4 angstrom
4. Show that the second excited state for a particle in a finite square well potential has energy greater than $\frac{2\hbar^2\pi^2}{mL^2}$ where m is the mass of the particle, L is the width of the potential and zero of the potential energy is taken at the bottom of the well.
5. Show that the difference between the ground state energy and the first excited state energy of a particle of mass m in a finite square well potential of width L must be greater than $\frac{3\hbar^2\pi^2}{2mL^2}$.
6. A particle of mass m moves in a potential that has the form shown in Figure 13.E1. It is ∞ for $x < 0$, 0 for $0 < x < L/2$, V_0 for $L/2 < x < L$ and ∞ for $x > L$. Obtain the equation satisfied by the energy eigenvalues E for $E > V_0$.

$$\textbf{Ans. } k \tan\frac{k_1 L}{2} + k_1 \tan\frac{kL}{2} = 0,\ k = \sqrt{\frac{2mE}{\hbar^2}},\ k_1 = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$$

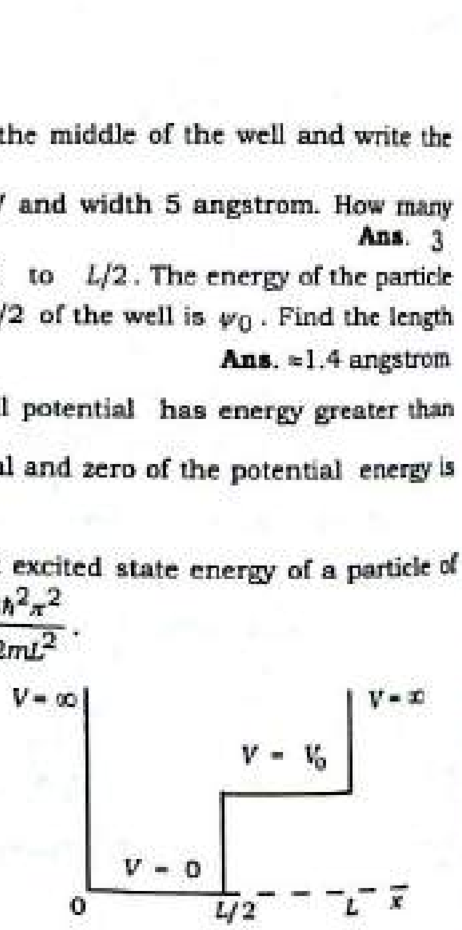

Fig. 13.E1

7. A particle of mass m is confined to a finite square well potential of length L with the bottom of the well taken as $V = 0$. The particle is found to be in a bound state with energy $\frac{2\pi^2\hbar^2}{9mL^2}$.

(a) Find the depth of the potential. (b) Show that the given energy is the ground state energy. **Ans.** (a) $\frac{8\pi^2\hbar^2}{9mL^2}$

8. A particle of mass m is confined to a finite square well from $x = -L/2$ to $x = L/2$. It is in its ground state and has the wave function $\psi = A$ at $x = 0$ and $\psi = \sqrt{3}\,A/2$ at $x = L/4$ at a particular instant. (a) Find the value of the wave function at $x = L/2$. (b) Find the ground state energy. (c) Find the depth of the well.

Ans. (a) $\frac{A}{2}$ (b) $\frac{2\pi^2\hbar^2}{9mL^2}$ (c) $\frac{8\pi^2\hbar^2}{9mL^2}$

9. A particle of mass m is subjected to a finite square well potential $V = 0$ for $|x| < \frac{L}{2}$, $V = V_0$ otherwise. In its ground state, the energy is found to be $E = \frac{\hbar^2\pi^2}{8mL^2}$. Find the value of x for which $\frac{\psi(x)}{\psi(L/2)} = \frac{1}{e}$.

Ans. $L\left(\frac{1}{2} + \frac{2}{\pi}\right)$

10. A particle moves under a finite square well potential of range $-\frac{L}{2} < x < \frac{L}{2}$. If the wave function at $x = L$ is A and at $x = 2L$ is $A/2$, what will be its value at $x = 4L$. **Ans.** $A/8$

11. A particle of mass m is placed in a finite square well potential $V = V_0$ for $|x| > L/2$, $V = 0$ for $|x| < L/2$. Show that the bound state energy values corresponding to the even wave functions satisfy $\cos\left(\frac{L}{2}\sqrt{\frac{2mE}{\hbar^2}}\right) = \sqrt{\frac{E}{V_0}}$ and corresponding to the odd wave functions satisfy $\sin\left(\frac{1}{2}\sqrt{\frac{2mE}{\hbar^2}}\right) = -\sqrt{\frac{E}{V_0}}$.

POSTSCRIPT

A quantum well

P13.1 What is a quantum Well?

The term "quantum well" is generally used for a semiconductor structure in which a very thin layer of a semiconductor material with low band gap is sandwitched between two thick layers of another semiconductor material with larger band gap. I have not told you about semiconductors or energy bands or band gaps, but I believe you are familiar with these terms, at least qualitatively. GaAs has a smaller band gap than GaAlAs. Suppose a thin layer of GaAs, of width L, is sandwitched between two thick layers of GaAlAs. Such a system is called a *hetero-junction* and has many applications in making optical sources such as lasers. What will be the structure of the conduction band and the valence band of this composite material? It is shown in Figure P13.1. Here E_g and E_g' are the band gaps for GaAlAs and GaAs respectively. The abbreviation V.B. is used for valence band and C.B. for conduction band. Consider a conduction electron in GaAlAs on the left. What are the energy values available to it? All energies greater than e_2 are available. I

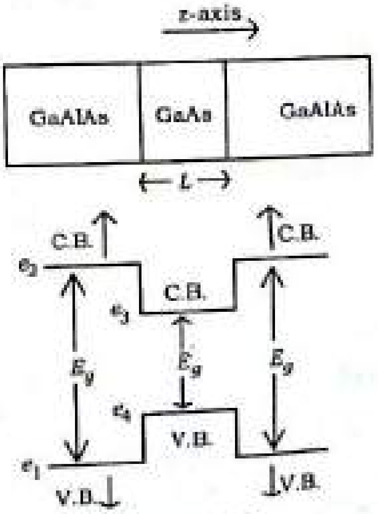

Fig. P13.1

am writing all energies because there is a large volume available to the electron in GaAlAs, it can go in all 3-dimensions freely. Similar is the case for a conduction electron in GaAlAs on right. But what are the energies available to a conduction electron in the GaAs region? Are all energies greater than e_3 (the bottom of conduction band of GaAs) allowed? The motion of the electron in the z-direction (left to right in Figure P13.1) is restricted. As it tries to enter from GaAs to GaAlAs, (on either side) there is a sudden increase in potential. So the electron finds itself in a finite square well potential. If the energy of the electron is greater than e_2 it is not bound. But for energy less than e_2 it is bound by the finite potential well of depth $V_0 = e_2 - e_3$ and width L.

All energies from e_3 to e_2 are not allowed. The allowed energy levels are discrete and finite in number. The number of energy levels in the bound state depends on the strength of the potential. It can be one, two, three or more depending upon $V_0 L^2$. The minimum is not at e_3.

But the energy of the electron is not just governed by its motion in the z-direction. The electron can move to large distances in the x, y directions. There is no confinement in these directions (confinement is in very large length you can say, in centimeters or so) and hence the energy corresponding to the motion in the x, y directions will vary continuously. So you have a system where the motion is almost free in x and y direction, but it is confined in the z-direction to a small interval. Such a structure is called a *quantum well*.

P13.2 Density of states in a quantum well

Let me model a quantum well by a 3-D box of length L, width L and height l (Figure P13.2). While L is very large, l is quite small. A particle in this box is free as long as it is inside the box. If it tries to come out of the box from x or y direction it finds an infinite potential which pushes it back into the box. But if it tries to come out from the z-direction, it encounters only a finite potential jump. So the potential can be written as

$$V = V(x) + V(y) + V(z)$$

where

$$V(x) = 0 \text{ for } 0 < x < L \text{ and } \infty \text{ otherwise}$$

$$V(y) = 0 \text{ for } 0 < y < L \text{ and } \infty \text{ otherwise}$$

$$V(z) = 0 \text{ for } 0 < z < l \text{ and } V_0 \text{ otherwise.}$$

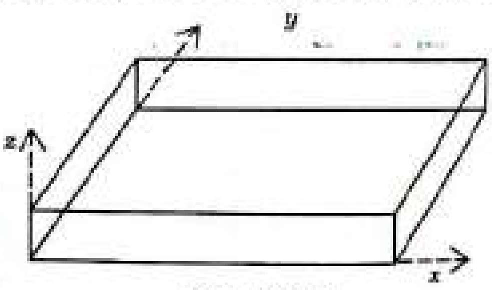

Fig. P13.2

Remember L is very large and l is very small. The kinetic energy operator is

$$K = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right).$$

The Hamiltonian is

$$\mathrm{H} = \mathrm{H}_1 + \mathrm{H}_2 + \mathrm{H}_3$$

where

$$\mathrm{H}_1 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

$$\mathrm{H}_2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + V(y)$$

and

$$\mathrm{H}_3 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + V(z).$$

The energy eigenvalues are given by,

$$E = E_1 + E_2 + E_3$$

where E_1, E_2, E_3 are eigenvalues of H_1, H_2, H_3 respectively. As L is quite large, the energy $E_1 + E_2$ will vary almost continuously with equal density of quantum states. This density of states will be $\frac{mh^2}{2\hbar^2\pi}$ per unit area as derived in the postscript of Chapter 12. Let me call it ρ. But E_3 has only finite number of values. Depending on the strength V_0l^2, it can be just one or two or more. Let me denote these eigenvalues as E'_1, E'_2, E'_3, etc.

How many energy eigenstates (quantum states) are there in the energy range E to $E + dE$? I have schematically shown the distribution of $E_1 + E_2$ and of E_3 in Figure P13.3. The minimum energy $E\,(= E_1 + E_2 + E')$ must be E'_1. So, there is no state available for energy 0 to E'_1. The density of states $g(E) = \frac{dN}{dE}$ is therefore zero for $0 < E < E'_1$. For energy E between E'_1 and E'_2, the value of E_3 can only be E'_1. The number of quantum states in the energy interval E to $E + dE$ is therefore $\rho\, dE$ and the density of states is ρ. Thus there is a sudden jump in the density of states (DOS) at the energy $E = E'_1$ (Figure P13.4).

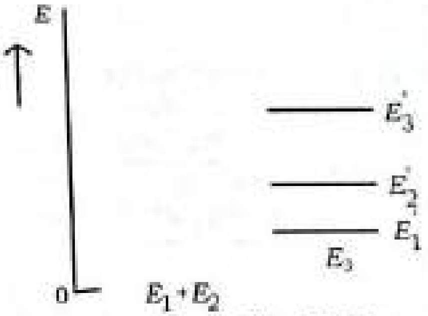

Fig. P13.3

Now consider the energy between E'_2 and E'_3, say $E = E'_2 + h$. This energy can be realized in two different manners,

(a) $E_3 = E'_2$, $E_1 + E_2 = h$

(b) $E_3 = E'_1$, $E_1 + E_2 = E_2 - E'_1 + h$.

The eigenfunctions corresponding to the situations (a) and (b) are quite different. For each state of kind (a), you also have a state of kind (b). Thus the number of quantum states in the interval E to $E + dE$ is $2\rho\, dE$ and the DOS is 2ρ.

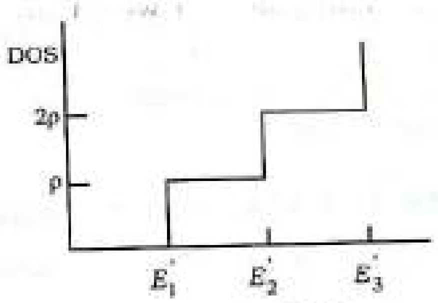

Fig. P13.4

Thus every time you cross the energy eigenvalues of H_3, the DOS jumps by ρ. The DOS varies with energy as a step function as shown in Figure P13.4.

18

Let us Rotate — Angular Momentum

So far, I have considered quantum mechanical systems involving essentially a single particle in one dimension. The space was only the x-axis. The idea behind spending so much time with a single particle in one dimension was to give you maximum opportunity to learn the basic structure of quantum mechanics which is so different from what we use in our common activities—the classical physics. Quantum systems are dealt with entirely new ideas and new tools such as description of the state of the particle by a wave function, of the measurable quantities by mathematical operators and so on. The procedure to get relevant information about physical quantities from the given wave function was also quite new. You also realized the importance of measurement processes. In particular, you saw that a measurement disturbs the system in a fundamental manner so that the wave function suddenly collapses to one of the eigenfunctions of the operator corresponding to the quantity measured. You also saw that the theory puts certain limits on the accuracy with which two quantities can be measured in the same state. The dynamics, that is the time evolution of the wave function, is governed by the Schrödinger equation.

Occasionally, I described some physical phenomena that need quantum mechanical description and which could be, at least in a crude approximation, dealt with a one-dimensional approximation. Alpha decay, field emission, etc., are examples. The main idea behind confining to one-dimensional situations was that I wanted to keep the mathematical complexities low so that you could devote maximum attention to the formulation of quantum mechanics. Now that you have gotten some experience in the theory of quantum mechanics, I wish to tackle three-dimensional problems. Angular momentum plays a key role in such problems and this chapter is mainly devoted to the general understanding of angular momentum in quantum mechanics. But before that a little bit on the appearance of wave functions and operators in three dimensions.

18.1 Wave functions and operators in three dimensions

In one-dimensional problems, the position of a particle is represented by a single coordinate x which is also the independent variable for writing the wave function $\psi(x)$. The operators are also written in terms of this variable x. These are either multiplication type (multiplication by a function of x) or differentiation type (differentiating once or more with respect to x). In three dimensions, the position of a particle is represented by three coordinates. If you use a Cartesian coordinate system, these coordinates are x, y and z. If you use a spherical polar coordinate system, the coordinates are r, θ and ϕ. I am sure you have studied about this coordinate system and hence will quickly refresh your memory using Figure 18.1. We still use three mutually perpendicular lines from the origin O and label them as x-, y-, z- axes. The distance of a point P from the origin is called its r-coordinate and the angle made by OP with the z-axis is called the θ-coordinate. The angle between the plane OPZ and XOZ is called the ϕ-coordinate. If you drop a perpendicular from P on the x-y plane which meets it at A, the angle XOA is the same as ϕ. For a given point, you can find a unique (r, θ, ϕ) in the range $0 \le r < \infty$, $0 \le \theta < \pi$, $0 \le \phi < 2\pi$. However, if you allow θ and ϕ to go beyond this range, two different sets of coordinates may correspond to the same point. For example, the point (r, θ, ϕ) is the same as $(r, \theta, \phi + 2\pi)$.

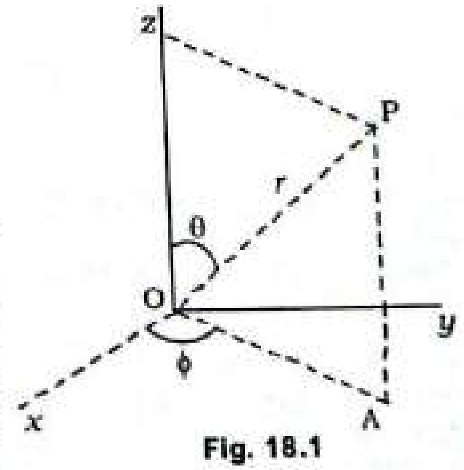

Fig. 18.1

The wave function of a particle is a function of its coordinates. So it can be written as $\psi(x, y, z)$ if Cartesian coordinates are used and $\psi(r, \theta, \phi)$ if spherical polar coordinates are used. If any other coordinate system is used the wave function is written as a function of the corresponding three coordinates. You can also write the wave function as $\psi(\mathbf{r})$. The operators are also written in terms of these coordinates. They may be of multiplication type or differentiation type. As more than one variable are involved in the wave function, partial derivatives are used. For example, the operator for kinetic energy written in Cartesian coordinates is

$$K = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right].$$

While differentiating $\psi(x, y, z)$ with respect to x, the coordinates y and z are treated as constants and so on. If spherical coordinates are used, partial derivatives with respect to r, θ, ϕ are used.

How do we define the scalar product of two wave functions in three dimensions? In one dimension I had given you the definition

$$\langle\psi_1|\psi_2\rangle = \int_{-\infty}^{\infty}\psi_1^*(x)\,\psi_2(x)\,dx\,.$$

The integration is on length x. The limits $-\infty, \infty$ denote that the integration is to be done over the whole space (which is only along the x-axis for one dimension). In three dimensions we have to integrate over the volume and cover the whole three-dimensional space. Writing volume element as $d\tau$, the scalar product of $\psi_1(\mathbf{r})$ with $\psi_2(\mathbf{r})$ is,

$$\langle\psi_1|\psi_2\rangle = \int_{\text{whole space}}\psi_1^*(\mathbf{r})\,\psi_2(\mathbf{r})\,d\tau\,.$$

In Cartesian coordinate system, $d\tau = dx\,dy\,dz$ and the wave function is in terms of x, y and z. So,

$$\langle\psi_1|\psi_2\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi_1^*(x,y,z)\,\psi_2(x,y,z)\,dx\,dy\,dz\,.$$

In spherical polar coordinates, the volume element is

$$d\tau = (dr)(r d\theta)(r\sin\theta\, d\phi) = r^2\sin\theta\, dr\, d\theta\, d\phi\,.$$

You can visualize this if you change r to $r + dr$, θ to $\theta + d\theta$ and ϕ to $\phi + d\phi$, one at a time, and see what kinds of lines are drawn from P in this process. The three variations give three mutually perpendicular lines (in infinitesimal approximation) PA, PB, PC of lengths dr, $r d\theta$ and $r\sin\theta\, d\phi$, and their product gives the volume element $d\tau$. The scalar product between two wave functions can therefore be written as

$$\langle\psi_1|\psi_2\rangle = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{\infty}\psi_1^*(r,\theta,\phi)\,\psi_2(r,\theta,\phi)\,r^2\sin\theta\, dr\, d\theta\, d\phi.$$

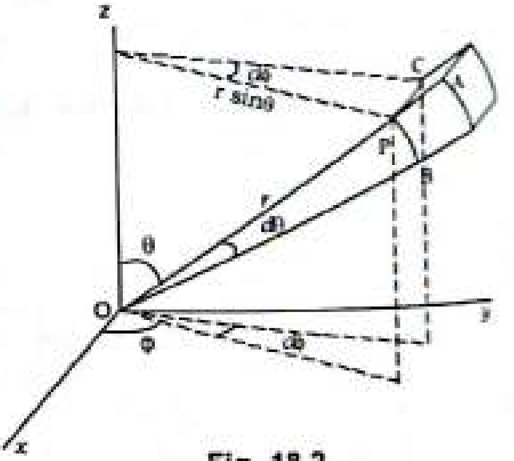

Fig. 18.2

If you take the scalar product of a wave function with itself, you get the square of the norm of this function. And if this quantity is equal to one, the wave function is called normalized.

18.2 Orbital angular momentum

In classical mechanics, Angular momentum is an important quantity in discussing motion of a particle under central forces or of a rotating body. You must have studied planetary motion around the Sun. The fact that angular momentum has a fixed direction leads to the result that the planetary orbits are all planar. The fact that the angular momentum has a constant magnitude leads to Kepler's second law which states that the radius vector from the Sun to the planet sweeps equal areas in equal times. In quantum mechanics too, angular momentum is a very important quantity to understand the behaviour of a particle under central potentials such as a hydrogen atom where the electron is attracted towards the proton by inverse square Coulomb attraction. Let us look at the operators corresponding to this physically measurable quantity angular momentum.

The angular momentum of a particle about a given point is defined in classical mechanics as $\mathbf{l} = \mathbf{r} \times \mathbf{p}$ where $\mathbf{r}$ is the position vector of the particle with the given point as the origin of the coordinate system and $\mathbf{p}$ is the linear momentum of the particle. Writing in the component form,

$$l_x = yp_z - zp_y, \quad l_y = zp_x - xp_z, \quad l_z = xp_y - yp_x .$$

What we know as angular momentum in classical mechanics, is called *orbital angular momentum* in quantum mechanics. The extra adjective "orbital" does not mean that the particle is going in an orbit. Any thing like a trajectory or an orbit is against the spirit of quantum mechanics. Angular momentum resulting from any kind of motion in space comes under orbital angular momentum.

The three quantities l_x, l_y, l_z are treated in quantum mechanics as dynamical variables and we define the corresponding Hermitian operators as

$$\begin{aligned} \mathrm{L_x} &= \mathrm{YP_z - ZP_y} \\ \mathrm{L_y} &= \mathrm{ZP_x - XP_z} \qquad (18.1) \\ \text{and,} \quad \mathrm{L_z} &= \mathrm{XP_y - YP_x} . \end{aligned}$$

Here X is the operator for the x-coordinate, Y for the y-coordinate and Z for the z-coordinate. These are multiplication type operators. X operating on a wave function $\psi(x, y, z)$ will multiply it by x and so on. The operators $\mathrm{P_x, P_y, P_z}$ represent the components of linear momentum and are differentiation type operators, operating on the wave functions. Thus

$$\mathrm{P_x} = -i\hbar\frac{\partial}{\partial x}, \quad \mathrm{P_y} = -i\hbar\frac{\partial}{\partial y} \text{ and } \mathrm{P_z} = -i\hbar\frac{\partial}{\partial z} .$$

Commutation relations

The angular momentum operators $\mathrm{L_x, L_y, L_z}$ obey the following commutation relations.

$$\left[\mathrm{L_x, L_y}\right] = i\hbar\mathrm{L_z}, \quad \left[\mathrm{L_y, L_z}\right] = i\hbar\mathrm{L_x}, \quad \left[\mathrm{L_z, L_x}\right] = i\hbar\mathrm{L_y} . \qquad (18.2)$$

Let me show the first of these.

$$\begin{aligned} \left[\mathrm{L_x, L_y}\right] &= \left[\mathrm{YP_z - ZP_y,\ ZP_x - XP_z}\right] \\ &= \left[\mathrm{YP_z - ZP_y, ZP_x}\right] - \left[\mathrm{YP_z - ZP_y, XP_z}\right] \\ &= \left[\mathrm{YP_z, ZP_x}\right] - \left[\mathrm{ZP_Y, ZP_x}\right] - \left[\mathrm{YP_z, XP_z}\right] + \left[\mathrm{ZP_y, XP_z}\right] \\ &= a - b - c + d . \qquad \text{(i)} \end{aligned}$$

$$\begin{aligned} a = \left[\mathrm{YP_z, ZP_x}\right] &= \mathrm{Y}\left[\mathrm{P_z, ZP_x}\right] + \left[\mathrm{Y, ZP_x}\right]\mathrm{P_z} \\ &= \mathrm{Y}\left\{\mathrm{Z}\left[\mathrm{P_z, P_x}\right] + \left[\mathrm{P_z, Z}\right]\mathrm{P_x}\right\} + \left\{\mathrm{Z}\left[\mathrm{Y, P_x}\right] + \left[\mathrm{Y, Z}\right]\mathrm{P_x}\right\}\mathrm{P_z} . \qquad \text{(ii)} \end{aligned}$$

Look at $\left[\mathrm{P_z, P_x}\right]$. Here $\mathrm{P_z}$ involves differentiation with respect to z and $\mathrm{P_x}$ involves differentiation with respect to x. For any wave function $\psi(x, y, z)$,

$$\frac{\partial}{\partial x}\left[\frac{\partial}{\partial z}\psi(x, y, z)\right] = \frac{\partial}{\partial z}\left[\frac{\partial}{\partial x}\psi(x, y, z)\right].$$

The order of differentiation is immaterial. Thus $\mathrm{P_x}$ and $\mathrm{P_z}$ commute and so $\left[\mathrm{P_z, P_x}\right] = 0$. The next commutator in equation (ii) is $\left[\mathrm{P_z, Z}\right]$ which is equal to $-i\hbar$. The next one is $\left[\mathrm{Y, P_x}\right]$. The operator Y involves multiplication by y and P_x involves differentiation with respect to x (treating y as constant). For any function $\psi(x, y, z)$,

$$\frac{\partial}{\partial x}\left[y\,\psi(x,y,z)\right] = y\frac{\partial}{\partial x}\psi(x,y,z).$$

So, Y and P_x commute and $[Y, P_x] = 0$. The last commutator in (ii) is [Y, X]. Both Y and X are multiplication type and hence commute. Thus $a = (-i\hbar)\,YP_x$.

There are three operators Z, P_x and P_y involved in the expression $[ZP_y, ZP_x]$ for b. All the three commute with each other. So they can be operated in any order and hence the above commutator is zero. Similar is the case with c and that is also zero.

$$\begin{aligned} d = \left[ZP_y, XP_z\right] &= Z\left[P_y, XP_z\right] + \left[Z, XP_z\right]P_y \\ &= Z\left[P_y, XP_z\right] + \left\{X[Z, P_z] + [Z, X]P_z\right\}P_y \\ &= 0 + \left\{X(i\hbar) + 0\right\}P_y = i\hbar XP_y. \end{aligned}$$

Thus from (i),

$$\left[L_x, L_y\right] = (-i\hbar)\,YP_x + i\hbar XP_y = i\hbar\left[XP_y - YP_x\right] = i\hbar L_z.$$

Once $[L_x, L_y]$ is evaluated, you can directly write the results for $[L_y, L_z]$ and $[L_z, L_x]$ by cyclically permuting x, y, z. Note that the definition of L_y and L_z in Equation 18.1 also follow from the cyclic permutation of x, y, z in the definition of L_x.

Thus the three operators L_x, L_y and L_z do not commute with each other. Hence, they do not have simultaneous eigenfunctions in general. If the particle has a wave function which is an eigenfunction of L_x, in general, it will not be an eigenfunction of L_y or L_z (I will mention one exception shortly). Thus if l_x is known precisely in a given state of the particle, you cannot know l_y or l_z precisely in that same state of particle. There is one exception to this result. It is possible to have a state in which $l_x = l_y = l_z = 0$. In this case all three components are precisely known.

The operator L^2

The quantity $l^2 = l_x^2 + l_y^2 + l_z^2$ denotes the square of the angular momentum in classical physics. In quantum mechanics too it is an important measurable quantity and we define a Hermitian operator

$$L^2 = L_x^2 + L_y^2 + L_z^2 \tag{18.3}$$

for it. You may wonder why do we define an operator for the square of the magnitude of angular momentum and not for the magnitude itself. The corresponding classical quantity is $l = [l_x^2 + l_y^2 + l_z^2]^{1/2}$. You know the meaning of squaring an operator (operating twice) and hence you can define L_x^2, L_y^2, L_z^2 and hence $L^2 = L_x^2 + L_y^2 + L_z^2$. But we have never defined how to take square root of an operator. So $L = \sqrt{L_x^2 + L_y^2 + L_z^2}$ is not a valid operator.

You can check the commutation relation of L^2 with any of the component operators L_x, L_y or L_z. Let me work out $[L^2, L_z]$.

$$\left[L^2, L_z\right] = \left[L_x^2, L_z\right] + \left[L_y^2, L_z\right] + \left[L_z^2, L_z\right]$$

$$= L_x[L_x, L_z] + [L_x, L_z]L_x + L_y[L_y, L_z] + [L_y, L_z]L_y + L_z[L_z, L_z] + [L_z, L_z]L_z$$
$$= -L_x[L_z, L_x] - [L_z, L_x]L_x + L_y[L_y, L_z] + [L_y, L_z]L_y$$
$$= -i\hbar L_x L_y - i\hbar L_y L_x + i\hbar L_y L_x + i\hbar L_x L_y$$
$$= 0.$$

Similarly, $\left[L^2, L_x\right] = \left[L^2, L_y\right] = 0$

So, L^2 commutes with each of the three operators L_x, L_y and L_z. It is possible to have definite values of l^2 and l_z in the same state. But it is not possible to have definite values of l_x and l_y in the same state, or of l_y and l_z in the same state, or of l_z and l_x in the same state (remember the exception).

18.3 Eigenvalues and eigenfunctions of the angular momentum operators

It is useful and easier to work in the spherical polar coordinates while writing the eigenfunctions of the angular momentum operators. You can write the expressions for L_x, L_y, L_z and L^2 in terms of the spherical polar coordinates using the definitions given in Equations 18.1 and 18.3, and the relations $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, $z = r\cos\theta$. The expressions are,

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right) \tag{18.4}$$

$$L_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right) \tag{18.5}$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}. \tag{18.6}$$

18.3.1 Eigenvalues and eigenfunctions of L_z

The expression for L_z turns out to be particularly simple. The eigenvalue equation for L_z is

$$\left(-i\hbar\frac{\partial}{\partial\phi}\right)f(r,\theta,\phi) = \mu f(r,\theta,\phi) \tag{i}$$

where $f(r,\theta,\phi)$ is an eigenfunction and μ is the corresponding eigenvalue. As the differentiation is with respect to ϕ, treat r, θ as constants. Equation (i) can then be written as,

$$\frac{df}{f} = \frac{i}{\hbar}\mu d\phi$$

or
$$f(r,\theta,\phi) = f_1\, e^{\frac{i}{\hbar}\mu\phi} \tag{ii}$$

where f_1 is the constant of integration. As r, θ were treated as constants in solving the differential equation, this constant f_1 can be a function of r and θ. Thus the eigenfunctions of L_z are

$$f(r,\theta,\phi) = f_1(r,\theta)e^{\frac{i}{\hbar}\mu\phi}. \tag{iii}$$

Are all values of μ allowed? No, there are some restrictions. As the point (r, θ, ϕ) is the same as the point $(r, \theta, \phi + 2\pi)$, the eigenfunction should not change if ϕ is changed to $\phi + 2\pi$. This is because there must be a unique value of the eigenfunction at a given point in the space. So

$$f(r,\theta,\phi) = f(r,\theta,\phi+2\pi).$$

Using this in (iii),

$$e^{\frac{i}{\hbar}\mu\phi} = e^{\frac{i}{\hbar}\mu(\phi+2\pi)}$$

or,

$$e^{i2\pi(\mu/\hbar)} = 1.$$

This is satisfied only if $\mu/\hbar$ is an integer. The eigenvalues of L_z are therefore,

$$\mu = m\hbar, \quad m = 0, \pm 1, \pm 2, \pm 3, \ldots \tag{18.7}$$

The eigenfunctions of L_z are

$$f(r,\theta,\phi) = f_1(r,\theta)e^{im\phi} \tag{18.8}$$

where m is an integer and $f_1(r,\theta)$ is an arbitrary function of r and θ. By choosing different functions $f_1(r,\theta)$ but keeping the part $e^{im\phi}$ unchanged, you can have infinite number of independent eigenfunctions of L_z with the same eigenvalue $m\hbar$. Thus, each eigenvalue of L_z is infinite-fold degenerate.

The eigenvalues of L_x and L_y are also $m\hbar$ with integral values of m. This is because all directions in space are equivalent and any direction can be chosen as the z-axis. The eigenfunctions of L_x, L_y do not have simple forms and I will not attempt to get them.

18.3.2 Eigenvalues and eigenfunctions of L^2

Now consider L^2. The expression in terms of the spherical polar coordinates is

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{18.9}$$

The eigenvalue equation for L^2 is

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]f(r,\theta,\phi) = \lambda f(r,\theta,\phi). \tag{i}$$

As L^2 and L_z commute they have a complete set of common eigenfunctions. It is therefore sufficient to look into the eigenfunctions of L_z and see which of them are also eigenfunctions of L^2. So write

$$f(r,\theta,\phi) = f_1(r,\theta)\,e^{im\phi} \tag{ii}$$

where m is an integer and the form of $f_1(r,\theta)$ is to be found so that $f(r,\theta,\phi)$ becomes an eigenfunction of L^2. Substituting from (ii) in (i),

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_1}{\partial\theta}\right) + \frac{\left(-m^2\right)f_1}{\sin^2\theta}\right]e^{im\phi} = \lambda f_1 e^{im\phi}$$

or

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\frac{\sin^2\theta}{\sin\theta}\frac{\partial f_1}{\partial\theta}\right) - \frac{m^2 f_1}{\sin^2\theta} + \frac{\lambda}{\hbar^2}f_1 = 0. \tag{iii}$$

Now define $x = \cos\theta$, so that $\sin\theta\, d\theta = -dx$. Equation (iii) can be written as

$$\frac{\partial}{\partial x}\left[\left(1-x^2\right)\frac{\partial f_1}{\partial x}\right]+\left(\frac{\lambda}{\hbar^2}-\frac{m^2}{1-x^2}\right)f_1=0$$

or

$$\left(1-x^2\right)\frac{\partial^2 f_1}{\partial x^2}-2x\frac{\partial f_1}{\partial x}+\left[\frac{\lambda}{\hbar^2}-\frac{m^2}{1-x^2}\right]f_1=0.$$

For the purpose of differentiation and integration, r is treated as constant and f_1 as a function x only. Thus for solving the equation, I can write it as,

$$\left(1-x^2\right)\frac{d^2 f_1}{dx^2}-2x\frac{df_1}{dx}+\left[\frac{\lambda}{\hbar^2}-\frac{m^2}{1-x^2}\right]f_1=0. \tag{iv}$$

This equation is very well studied by mathematicians and is called *associated Legendre equation*. If $m = 0$, the equation is called *Legendre equation*. I have given the steps to solve these equations in Appendix-3. The important result is that the solution diverges as $x \to 1$ (that is, $\theta \to 0$) unless $\lambda/\hbar^2$ is a product of two successive nonnegative integers l and $(l+1)$, and $l \geq |m|$. As the eigenfunction should not diverge for any value of θ, we must have

$$\frac{\lambda}{\hbar^2}=l(l+1)$$

or

$$\lambda=l(l+1)\hbar^2, \quad l=m, m+1, m+2, \dots . \tag{18.10}$$

Allowing all values of m, i.e., $m = 0, \pm 1, \pm 2, \dots$, the eigenvalues of L^2 are $0, 2\hbar^2, 6\hbar^2, 12\hbar^2$, etc. For a given l and m, the solution of equation (iv) is

$$f_1(x)=A\,P_l^m(x) \tag{v}$$

where $P_l^m(x)$ is a function called *associated Legendre function* and has a specific form. The constant A is arbitrary for this integration. As r has been treated as a constant in solving equation (iv), so A can be taken as an arbitrary function of r. I write this as $f_2(r)$. Also write $x = \cos\theta$. Then (v) is same as,

$$f_1(r,\theta)=f_2(r)\,P_l^m(\cos\theta).$$

Thus the eigenfunction of L^2 (and also of L_z) are $f_2(r)P_l^m(\cos\theta)e^{im\phi}$.

The functions $P_l^m(\cos\theta)e^{im\phi}$ with proper normalization constant are called *spherical harmonics* and are written as $Y_l^m(\theta,\phi)$. The normalization constant is fixed by the requirement

$$\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\left|Y_l^m(\theta,\phi)\right|^2\sin\theta\,d\theta\,d\phi=1.$$

The common eigenfunctions of L^2 and L_z can therefore be written as,

$$f(r,\theta,\phi)=f_2(r)\,Y_l^m(\theta,\phi).$$

Table 18.1 gives $P_l^m(\cos\theta)$ and $Y_l^m(\theta,\phi)$ for some values of l and m. The expressions for $P_l^m(\cos\theta)$ are not normalized and only give the dependence on θ. On the other hand, the expressions for $Y_l^m(\theta,\phi)$ are normalized.

Degeneracy

The functions $f_2(r)\,Y_l^m(\theta,\phi)$ are the simultaneous eigenfunctions of L^2 and L_z. As $f_2(r)$ can take any arbitrary form, the eigenvalues of L^2 are also infinite-fold degenerate. If you focus only on the θ, ϕ part, the degeneracy is finite. There is only one eigenfunction corresponding to the eigenvalue 0 ($l = 0$) and that is just a constant (see Table 18.1). You can say that in θ-ϕ space this eigenvalue of L^2 is nondegenerate. The eigenvalue $2\hbar^2$ (l = 1) is 3-fold degenerate in θ-ϕ space as there are three different eigenfunctions $Y_l^m(\theta,\phi)$ corresponding to m = 0, ± 1. In general, the eigenvalue $l(l+1)\hbar^2$ is $(2l+1)$-fold degenerate as m can take $(2l+1)$ values 0, ± 1, ..., ± l, and each m gives a different eigenfunction. The quantities l and m are called *orbital angular momentum quantum numbers*. The quantum state which is simultaneous eigenfunction of L^2 and L_z is written as $|lm\rangle$. Indeed it is not a total description of the state, as L^2, L_z only relate to orbital angular momentum part. The wave

Table 18.1

l	m	Eigenvalue of L^2	Eigenvalue of L_z	$P_l^m(\cos\theta)$ (not normalized))	$Y_l^m(\theta,\phi)$
0	0	0	0	1	$\frac{1}{\sqrt{4\pi}}$
1	1	$2\hbar^2$	$\hbar$	$\sin\theta$	$-\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}$
1	0	$2\hbar^2$	0	$\cos\theta$	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	−1	$2\hbar^2$	$-\hbar$	$\sin\theta$	$\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi}$
2	2	$6\hbar^2$	$2\hbar$	$\sin^2\theta$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\phi}$
2	1	$6\hbar^2$	$\hbar$	$\sin\theta\cos\theta$	$-\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{i\phi}$
2	0	$6\hbar^2$	0	$3\cos^2\theta-1$	$\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right)$
2	−1	$6\hbar^2$	$-\hbar$	$\sin\theta\cos\theta$	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\phi}$
2	−2	$6\hbar^2$	$-2\hbar$	$-\sin^2\theta$	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\phi}$

function can be $f(r)Y_l^m(\theta,\phi)$ for any $f(r)$. But when I write $|lm\rangle$, I give you the orbital angular momentum uniquely, values of L^2 and L_z.

Orthogonality

The spherical harmonics $Y_l^m(\theta,\phi)$ are orthogonal to each other. You complex conjugate the first function, multiply by the second, and integrate over entire solid angle to get the scalar product.

$$\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} Y_{l_1}^{m_1 *}(\theta,\phi)\, Y_{l_2}^{m_2}(\theta,\phi)\sin\theta\, d\theta\, d\phi = \delta_{l_1 l_2}\,\delta_{m_1 m_2}$$

If $l_1 \neq l_2$ or $m_1 \neq m_2$, the scalar product of $Y_{l_1}^{m_1}(\theta,\phi)$ with $Y_{l_2}^{m_2}(\theta,\phi)$ is zero. In fact the functions $Y_l^m(\theta,\phi)$ form an orthogonal basis for the θ-ϕ space. This means, any function $f(\theta,\phi)$, which may be useful to us, can be written as a linear combination of these functions.

$$f(\theta,\phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} A_{l,m} Y_l^m(\theta,\phi) \tag{18.11}$$

where $A_{l,m}$ are the expansion coefficients.

18.4 Generalized definition of angular momentum

The quantum mechanical operators L_x, L_y, L_z correspond to the measurable quantities l_x, l_y, l_z which are components of $\mathbf{r}\times\mathbf{p}$. Also, each of these operators has a specific form in terms of the coordinates. These operators obey specific commutation relations given by Equation 18.2. In quantum mechanics, these commutation relations themselves are taken as the definition of angular momentum. If there are three operators J_x, J_y, J_z which satisfy the commutation relation

$$\left[J_x, J_y\right] = i\hbar J_z,\quad \left[J_y, J_z\right] = i\hbar J_x,\quad \left[J_z, J_x\right] = i\hbar J_y$$

we will call J_x, J_y, J_z as some kind of angular momentum operators even if they do not have the specific form in θ, ϕ as described above. The operators L_x, L_y, L_z defined in terms of θ, ϕ follow these commutation relations and so qualify for being called angular momentum operators. Are there other sets of operators satisfying these commutation relations? The answers is "yes" and they represent a different kind of angular momentum not represented by $\mathbf{r}\times\mathbf{p}$. I will devote the next chapter completely on this "other variety" of angular momentum, but the next section gives you the method of finding the eigenvalues of angular momentum operators without using any specific form of the operators and relying only on the commutation relation.

18.5 Eigenvalues of J^2, J_z from commutation relations

The scheme to find the eigenvalues of J^2 and J_z is to some extent similar to what we did to find the eigenvalues of a linear harmonic oscillator. I will define raising and lowering operators, and use various commutation relations to get the eigenvalues. It will be a long procedure so have patience and enjoy. I assume that I am given three operators J_x, J_y, J_z obeying the commutation relations of angular momentum components. The operator J^2 is defined as $J^2 = J_x^2 + J_y^2 + J_z^2$ and commutes with each of the three component operators.

(a) All eigenvalues of J^2 are nonnegative

Let $|\psi\rangle$ represent the state of the particle at the given time. I can write,

$$\langle\psi|J^2|\psi\rangle = \langle\psi|J_x^2|\psi\rangle + \langle\psi|J_y^2|\psi\rangle + \langle\psi|J_z^2|\psi\rangle.$$

Let $\qquad |\phi\rangle = J_x|\psi\rangle.$

Then $\qquad \langle\phi|\phi\rangle = \langle J_x\psi|J_x\psi\rangle = \langle\psi|J_xJ_x\psi\rangle = \langle\psi|J_x^2|\psi\rangle.$

I have used the Hermitian property of J_x in writing $\langle\psi|J_xJ_x\psi\rangle$ in place of $\langle J_x\psi|J_x\psi\rangle$. But $\langle\phi|\phi\rangle$ is the square of the norm of $|\phi\rangle$ and hence is a nonnegative quantity. So, $\langle\psi|J_x^2|\psi\rangle$ is nonnegative. Similarly $\langle\psi|J_y^2|\psi\rangle$ and $\langle\psi|J_z^2|\psi\rangle$ are also nonnegative, and so $\langle\psi|J^2|\psi\rangle$ is nonnegative for all $|\psi\rangle$. If I take $|\psi\rangle$ to be the eigenstate of J^2 corresponding to the eigenvalue λ,

$$\langle\psi|J^2|\psi\rangle = \lambda\langle\psi|\psi\rangle = \lambda.$$

Hence λ is nonnegative.

(b) The state $|j\,m\rangle$

Let me write the eigenvalue λ of J^2 as $j(j+1)\hbar^2$ where j is some number. The angular momentum has the same dimension as that of $\hbar$. So the eigenvalues of J^2 must have the same dimension as $\hbar^2$. Thus j must be a pure number. At this stage, I do not know (I pretend to do so) whether j is an integer or a half integer or something else. But for a given λ there is a unique nonnegative value of j. This can be seen as follows.

Let $\qquad \lambda = j(j+1)\hbar^2$

then, $\qquad j^2 + j - \frac{\lambda}{\hbar^2} = 0$

or, $\qquad j = \frac{-1 \pm \sqrt{1 + 4\lambda/\hbar^2}}{2}.$

One of the two values is necessarily negative which I reject. The other value is necessarily nonnegative and I accept this value. Then there is one to one correspondence between λ and j.

J_z has the dimension of $\hbar$. So I write the eigenvalues of J_z as $m\hbar$ where m is a pure number. At this stage I do not know whether m is positive, or negative, or integer, or fraction. I only know that it is a dimensionless number. As J^2 and J_z commute, they have a complete set of common eigenstates. Consider such a common eigenstate and suppose it corresponds to the eigenvalue $j(j+1)\hbar^2$ of J^2 and $m\hbar$ of J_z. This state is generally written as $|j\,m\rangle$ or $|j,m\rangle$. I also assume that the eigenstates represented by $|j\,m\rangle$ are normalized. I assume that in the space relevant to J^2 and J_z, I can write a unique eigenstate once j and m are given. Thus

$$J^2|j\,m\rangle = j(j+1)\hbar^2|j\,m\rangle$$

and $\qquad J_z|j\,m\rangle = m\hbar|j\,m\rangle.$

(c) The raising and lowering operators

Define operators

$$J_+ = J_x + iJ_y$$

and $$J_- = J_x - iJ_y\,.$$

These are called raising and lowering operators for angular momentum. These are not Hermitian operators but are adjoint of each other. Let me work out some expressions involving these operators.

Commutation relation with J_z

$$\left[J_z, J_+\right] = \left[J_z, J_x + iJ_y\right] = \left[J_z, J_x\right] + i\left[J_z, J_y\right] = i\hbar J_y + i(-i\hbar)J_x = \hbar\left(J_x + iJ_y\right) = \hbar J_+$$

$$\left[J_z, J_-\right] = \left[J_z, J_x - iJ_y\right] = \left[J_z, J_x\right] - i\left[J_z, J_y\right] = i\hbar J_y - i(-i\hbar)J_x = -\hbar\left(J_x - iJ_y\right) = -\hbar J_-$$

$$\left[J^2, J_+\right] = \left[J^2, J_x + iJ_y\right] = \left[J^2, J_x\right] + i\left[J^2, J_y\right] = 0$$

$$\left[J^2, J_-\right] = \left[J^2, J_x - iJ_y\right] = \left[J^2, J_x\right] - i\left[J^2, J_y\right] = 0\,.$$

The state $J_+|j\,m\rangle$

Let $|j\,m\rangle$ be an eigenstate of J^2 with eigenvalue $j(j+1)\hbar^2$ and of J_z with eigenvalue $m\hbar$. I will show that $J_+|j\,m\rangle$ is also an eigenstate of J^2 and J_z. As J^2 commutes with J_+,

$$J^2\left[J_+|j\,m\rangle\right] = J_+[J^2|j\,m\rangle] = J_+[j(j+1)\hbar^2|j\,m\rangle] = j(j+1)\hbar^2[J_+|j\,m\rangle]\,.$$

This shows that $J_+|j\,m\rangle$ is an eigenstate of J^2 with eigenvalue $j(j+1)\hbar^2$.

Next, let me show you the action of J_z on $J_+|j\,m\rangle$.

$$J_z\left[J_+|j\,m\rangle\right] = [J_zJ_+]|j\,m\rangle \tag{i}$$

We have, $\left[J_z, J_+\right] = \hbar J_+$.

This gives, $J_zJ_+ - J_+J_z = \hbar J_+$

or, $J_zJ_+ = J_+J_z + \hbar J_+$.

Substituting this in (i),

$$J_z\left[J_+|j\,m\rangle\right] = \left(J_+J_z + \hbar J_+\right)|j\,m\rangle = J_+\left(J_z|j\,m\rangle\right) + \hbar J_+|j\,m\rangle = m\hbar J_+|j\,m\rangle + \hbar J_+|j\,m\rangle$$

or, $$J_z\left[J_+|j\,m\rangle\right] = (m+1)\hbar\left[J_+|j\,m\rangle\right].$$

Thus $J_+|j\,m\rangle$ is an eigenstate of J_z with eigenvalue $(m+1)\hbar$. The state $|j\,m\rangle$ itself was an eigenstate of J_z with eigenvalue $m\hbar$. So the action of J_+ on $|j\,m\rangle$ is to give a new state which is an eigenstate of J_z with the eigenvalue raised by one unit ($\hbar$) and which is also an eigenstate of J^2 with the same eigenvalue $j(j+1)\hbar^2$. From these results I can say that

$$J_+|j\,m\rangle = c_1|j\;m+1\rangle \tag{ii}$$

where c_1 is some constant. Let me evaluate this constant by taking the scalar product with itself on both sides of (ii). The scalar product of the right hand side with itself is $|c_1|^2$ because $|j\;m+1\rangle$ is normalized. Thus,

$$|c_1|^2 = \left(\langle J_+|j\,m\rangle\middle|\left(J_+|j\,m\rangle\right)\right)$$

$$=\left(\left(\langle j\, m|\right)\left(J_-J_+|\,j\, m\rangle\right)\right) \qquad \text{(as } J_- \text{ is the Hermitian adjoint of } J_+\text{)}$$

$$=\langle j\, m|J_-J_+|\,j\, m\rangle. \tag{iii}$$

Also,
$$J_-J_+=\left(J_x-iJ_y\right)\left(J_x+iJ_y\right)$$
$$=J_x^2+J_y^2+i(J_xJ_y-J_yJ_x)$$
$$=J_x^2+J_y^2+i(i\hbar)J_z\ =J^2-J_z^2-\hbar J_z.$$

So by (iii),
$$|c_1|^2=\left\langle j\, m\left|J^2-J_z^2-\hbar J_z\right|j\, m\right\rangle$$
$$=\left\langle j\, m\left|J^2\right|j\, m\right\rangle-\left\langle j\, m\left|J_z^2\right|j\, m\right\rangle-\hbar\langle j\, m|J_z|\,j\, m\rangle$$
$$=j(j+1)\hbar^2-m^2\hbar^2-m\hbar^2$$
$$=\left[\left(j^2-m^2+(j-m)\right)\right]\hbar^2.$$

Thus,
$$|c_1|^2=(j-m)(j+m+1)\hbar^2$$

or
$$c_1=\sqrt{(j-m)(j+m+1)}\,\hbar. \tag{18.12}$$

I have chosen the real positive value for c_1. So,
$$J_+|\,j\, m\rangle=\sqrt{(j-m)(j+m+1)}\,\hbar\,|\,j\ \ m+1\rangle. \tag{18.13}$$

The state $J_-|\,j\, m\rangle$

Do a parallel calculation for $J_-|\,j\, m\rangle$. You will find that this is an eigenstate of J^2 with eigenvalue $j(j+1)\hbar^2$ and of J_z with eigenvalue $(m-1)\hbar$. Let me show it explicitly.

As J^2 commutes with J_-,
$$J^2\left[J_-|\,j\, m\rangle\right]=J_-[J^2|\,j\, m\rangle]=J_-[j(j+1)\hbar^2|\,j\, m\rangle]=j(j+1)\hbar^2[J_-|\,j\, m\rangle].$$

This shows that $J_-|\,j\, m\rangle$ is an eigenstate of J^2 with eigenvalue $j(j+1)\hbar^2$.

Next, look at the action of J_z on $J_-|\,j\, m\rangle$.
$$J_z\left[J_-|\,j\, m\rangle\right]=[J_zJ_-]|\,j\, m\rangle. \tag{iv}$$

We have,
$$[J_z,J_-]=-\hbar J_-.$$

This gives,
$$J_zJ_--J_-J_z=-\hbar J_-$$

or,
$$J_zJ_-=J_-J_z-\hbar J_-.$$

Substituting this in (iv),
$$J_z\left[J_-|\,j\, m\rangle\right]=(J_-J_z-\hbar J_-)|\,j\, m\rangle\ =J_-\left(J_z|\,j\, m\rangle\right)-\hbar J_-|\,j\, m\rangle\ =m\hbar J_-|\,j\, m\rangle-\hbar J_-|\,j\, m\rangle$$

or,
$$J_z\left[J_-|\,j\, m\rangle\right]=(m-1)\hbar\left[J_-|\,j\, m\rangle\right].$$

Thus $J_-|\,j\, m\rangle$ is an eigenstate of J_z with eigenvalue $(m-1)\hbar$. The state $|\,j\, m\rangle$ itself was an eigenstate of J_z with eigenvalue $m\hbar$. So the action of J_- on $|\,j\, m\rangle$ is to give a new state which is an eigenstate of

J_z with the eigenvalue lowered by one unit ($\hbar$) and which is also an eigenstate of J^2 with the same eigenvalue $j(j+1)\hbar^2$. From these results I can say that

$$J_-|j\ m\rangle = c_2|j\ \ m-1\rangle \tag{v}$$

where c_2 is some constant. As was done earlier, evaluate this constant by taking the scalar product with itself on both sides of (v). The scalar product of the right hand side with itself is $|c_2|^2$ because $|j\ m-1\rangle$ is normalized. Thus,

$$\begin{aligned}|c_2|^2 &= \left(\left(J_-|j\ m\rangle\right)\middle|\left(J_-|j\ m\rangle\right)\right)\\ &= \left(\left(\langle j\ m|\right)\left(J_+J_-|j\ m\rangle\right)\right) \qquad \text{[as } J_+ \text{ is the Hermitian adjoint of } J_-\text{]}\\ &= \langle j\ m|J_+J_-|j\ m\rangle.\end{aligned} \tag{vi}$$

Also,

$$\begin{aligned}J_+J_- &= \left(J_x + iJ_y\right)\left(J_x - iJ_y\right)\\ &= J_x^2 + J_y^2 - i(J_xJ_y - J_yJ_x)\\ &= J_x^2 + J_y^2 - i(i\hbar)J_z \ = J^2 - J_z^2 + \hbar J_z.\end{aligned}$$

So by (vi),

$$\begin{aligned}|c_2|^2 = \left\langle j\ m\middle|J^2 - J_z^2 + \hbar J_z\middle|j\ m\right\rangle &= \left\langle j\ m\middle|J^2\middle|j\ m\right\rangle - \left\langle j\ m\middle|J_z^2\middle|j\ m\right\rangle + \hbar\left\langle j\ m\middle|J_z\middle|j\ m\right\rangle\\ &= j(j+1)\hbar^2 - m^2\hbar^2 + m\hbar^2\\ &= \left[\left(j^2 - m^2 + (j+m)\right)\right]\hbar^2.\end{aligned}$$

Thus,

$$|c_2|^2 = (j+m)(j-m+1)\hbar^2$$

or

$$c_2 = \sqrt{(j+m)(j-m+1)}\ \hbar. \tag{18.14}$$

I have chosen the real, positive value for c_2. So,

$$J_-|j\ m\rangle = \sqrt{(j+m)(j-m+1)}\ \hbar|j\ \ m-1\rangle. \tag{18.15}$$

Now you know why J_+ and J_- are called raising and lowering operators.

(d) $-j \le m \le j$

From Equation 18.12 $|c_1|^2 = (j-m)(j+m+1)\hbar^2$, so,

$$(j-m)(j+m+1) \ge 0. \tag{vii}$$

The first factor is zero at $m = j$, and the second at $m = -j-1$. Remember, $j \ge 0$. Let us consider three cases, namely, $m < -j-1$, $-j-1 \le m \le j$ and $m > j$.

If $m < -j-1$, you have m negative making the first factor positive. The condition also ensures that the second factor is negative. Thus condition (vii) is not satisfied.

Now consider the case $-j-1 \le m \le j$. The relation $-j-1 \le m$ gives $0 \le j+m+1$. The second factor in (vii) is therefore zero or positive. Also as $m \le j$ the first factor $j-m$ is zero or positive. Hence condition (vii) is satisfied in this case.

If $m > j$, the first factor is negative and the second is positive so condition (vii) is not satisfied.

Thus condition (vii) is satisfied only when

$$-(j+1) \le m \le j. \tag{viii}$$

Now consider Equation 18.14. As $|c_2|^2 = (j+m)(j-m+1)\hbar^2$,

$$(j+m)(j-m+1) \ge 0. \tag{ix}$$

The first factor is zero at $m=-j$, and the second at $m=j+1$. Let us consider three cases, namely, $m<-j$, $-j \le m \le j+1$ and $m>j+1$.

If $m<-j$, you have $m+j<0$. So, the first factor is negative. However m itself is negative in this case and so the second factor is positive. Thus condition (ix) is not satisfied.

Now consider the case $-j \le m \le j+1$. The relation $-j \le m$ gives $0 \le j+m$. Thus, the first factor $j+m$ is zero or positive. Also as $m \le j+1$, you have $0 \le j-m+1$. The second factor in (ix) is therefore zero or positive. Hence condition (ix) is satisfied in this case.

If $m>j+1$, the first factor is positive and the second is negative. So condition (ix) is not satisfied. Thus condition (ix) is satisfied only when

$$-j \le m \le j+1. \tag{x}$$

Equations (viii) and (x) should both be satisfied. This is possible only if

$$-j \le m \le j. \tag{18.16}$$

(e) $J_+|j\ j\rangle$ and $J_-|j\ -j\rangle$

Now you know that m has to be between $-j$ and j. Suppose $m=j$ is a possible value. What happens if I apply the raising operator to the state $|j\ j\rangle$ where m is already at its highest value j? Just look at Equation 18.12. The quantity c_1 is the norm of $J_+|j\ m\rangle$. If you put $m=j$ in this equation, you get that the norm of $J_+|j\ j\rangle = 0$. Now suppose $m=-j$ is a possible value. What happens if I apply the lowering operator to the state $|j\ -j\rangle$ where m is already at its lowest value $-j$? Equation 18.14 gives that the norm of $J_-|j\ -j\rangle = 0$. Thus,

$$J_+|j\ j\rangle = J_-|j\ -j\rangle = 0. \tag{18.17}$$

A wave function with zero norm is not meaningful in quantum mechanics. A wave function with value zero everywhere in space tells that you have no chance of finding the particle in whole of the space. This is not a meaningful wave function for a particle. So J_+ operating on $|j\ j\rangle$ does not give you a state proportional to $|j\ j+1\rangle$ as you may think from the "raising" property of J_+. This is consistent with the fact that m cannot be greater than j.

Similarly J_- operating on $|j\ -j\rangle$ does not give a state proportional to $|j\ -j-1\rangle$. J_- does not lower the eigenvalue of J_z if m already has its minimum value $-j$.

(f) j, m can be either integers or half integers

This is the last subsection before I get the eigenvalues of J^2 and J_z. Suppose there is an eigenstate $|j\ m\rangle$. I can generate new eigenstates $|j\ m-1\rangle, |j\ m-2\rangle$, etc., by operating successively J_-. But if I continue this, at some stage I will get an eigenstate with values of m less than $-j$. But that is not possible. You cannot have a $|j\ m\rangle$ with m less than $-j$. The only way out is that the sequence m, $m-1$, $m-2$,.... reaches $-j$. In this case you get an eigenstate $|j\ -j\rangle$ and the application of J_- does not reduce the m value further, rather it gives zero.

Next operate J_+ on $|j\, m\rangle$ successively to generate new eigenstates $|j\ m+1\rangle$, $|j\ m+2\rangle$, $|j\ m+3\rangle$, etc. If I continue this, at some stage I will get an eigenstate with value of m greater than j unless the sequence m, $m+1, m+2$, $m+3, \ldots$ reaches j. If it does so, I get the eigenstate $|j\ j\rangle$ and any further application of J_+ will give zero state.

So by reducing m in steps of 1 one should reach $-j$ at some stage and by increasing m in steps of 1, one should reach $+j$ at some stage. This is only possible if $2j$ is an integer. So j must be either an integer or a half integer. If j is an integer m should also be an integer because the sequence $m+1$, $m+2, \ldots$, should reach j at some stage. Similarly if j is a half integer, m should also be a half integer.

Thus the commutation relations allow for half integral as well as integral angular momentum quantum numbers. The possible values of the eigenvalues of angular momentum square are $j(j+1)\hbar^2$ where j can be an integer or a half integer. But if I consider $\mathbf{r} \times \mathbf{p}$ as the definition of angular momentum, the eigenvalues of angular momentum square are $j(j+1)\hbar^2$ where j can only be an integer. This suggests that we may have another variety of angular momentum, not related to the motion of the particle in space and not known in classical physics, which correspond to half integral angular momentum quantum numbers. This other variety of angular momentum does exist and will be the main topic of the next chapter.

18.6 You learned in this chapter

- The wave function of a particle in three dimensions is written as $\psi(\mathbf{r})$, $\psi(x, y, z)$, $\psi(r, \theta, \phi)$, etc., where the symbols have their usual meanings.
- The scalar product of two functions $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ is defined as

  $$\langle\psi_1|\psi_2\rangle = \int_{\text{all space}} \psi_1(\mathbf{r})\,\psi_2(\mathbf{r})\,d\tau$$

  where $d\tau$ is the volume element at the position $\mathbf{r}$. If spherical coordinates are used, it is

  $$\langle\psi_1|\psi_2\rangle = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{\infty} r^2\psi_1^*(\mathbf{r})\,\psi_2(\mathbf{r})\sin\theta\,dr\,d\theta\,d\phi.$$

- The operators for the x, y, z components of orbital angular momentum $\mathbf{r} \times \mathbf{p}$ are

  $$L_x = YP_z - ZP_y$$
  $$L_y = ZP_x - XP_z$$
  $$L_z = XP_y - YP_x.$$

- $L_z = -i\hbar\dfrac{\partial}{\partial\phi}$ and $L^2 = -\hbar^2\left[\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial}{\partial\theta}\right) + \dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\phi^2}\right]$.
- $[L_x, L_y] = i\hbar\, L_z$, $[L_y, L_z] = i\hbar\, L_x$, $[L_z, L_x] = i\hbar\, L_y$.
- L_z has eigenvalues $m\hbar$ where $m = 0, \pm 1, \pm 2, \ldots$ and L^2 has eigenvalues $l(l+1)\hbar^2$ where $l = 0, 1, 2, \ldots$. For a simultaneous eigenfunction of L^2 and L_z, $m \le l$.
- The simultaneous eigenfunctions of L^2 and L_z, can be written as $\phi(r, \theta, \phi) = f(r)\, Y_l^m(\theta, \phi)$ where $f(r)$ is an arbitrary function of r and $Y_l^m(\theta, \phi)$ are the spherical harmonics.
- The spherical harmonics $Y_l^m(\theta, \phi)$ can be written as

$$Y_l^m(\theta,\phi) = P_l^m(\cos\theta)\,e^{im\phi}$$

where $P_l^m(\cos\theta)$ is the associated Legendre function. For $l = 0$, $m = 0$, the spherica harmonic is just a constant, independent of θ and ϕ.

- Spherical harmonics are orthogonal to each other and form a complete set in $(\theta, \phi$ space. Any function of θ and ϕ may be written as a linear combination of spherica harmonics.
- Any three operator J_x, J_y, J_z satisfying the commutation relations

$$\left[J_x, J_y\right] = i\hbar\, J_z, \quad \left[J_y, J_z\right] = i\hbar\, J_x, \quad \left[J_z, J_x\right] = i\hbar\, J_y$$

are called angular momentum operators in quantum mechanics.

- The possible eigenvalues of $J^2 = J_x^2 + J_y^2 + J_z^2$ and J_z, allowed by the commutation relation, are $j(j+1)\hbar^2$ and $m\hbar$ where j can be any nonnegative integer or half integer and m can take any value from $-j$ to $+j$ in steps of 1.

Solved Problems

1. Simplify the commutators (a) $[P_x, L_x]$ and (b) $[P_x, L_y]$.

***Solution:* (a)** $$[P_x, L_x] = [P_x, YP_z - ZP_y] = [P_x, YP_z] - [P_x, ZP_y].$$

Any two of P_x, Y and P_z commute with each other. So any combination of these will commute with any other combination. So the first commutator $[P_x, YP_z] = 0$. Similarly, P_x, Z and P_y commute with each other. So the second commutator $[P_x, ZP_y]$ is also zero. So, $[P_x, L_x] = 0$.

(b) $$[P_x, L_y] = [P_x, ZP_x - XP_z] = [P_x, ZP_x] - [P_x, XP_z].$$

The first commutator involves only two operators Z and P_x and they commute. Hence it is zero. The second commutator has P_x, X, P_z. As X and P_x do not commute, this commutator may not be zero.

$$[P_x, L_y] = -[P_x, XP_z] = -X[P_x, P_z] - [P_x, X]P_z = 0 + i\hbar\, P_z.$$

Thus $$[P_x, L_y] = i\hbar\, P_z.$$

2. Which of the following are eigenfunctions of L_z? For the cases where the function is an eigenfunction of L_z, find the corresponding eigenvalue.

(a) $\sin\theta e^{i\phi}$ (b) $e^{i(\theta+\phi)}$ (c) $e^{i\theta}\sin\phi$ (d) $r^n\cos\theta$

Solution: $L_z = -i\hbar\dfrac{\partial}{\partial\phi}$.

(a) $$-i\hbar\frac{\partial}{\partial\phi}\left(\sin\theta e^{i\phi}\right) = (-i\hbar)\sin\theta(i)e^{i\phi} = \hbar\sin\theta e^{i\phi}.$$

So $\sin\theta e^{i\phi}$ is an eigenfunction of L_z and the corresponding eigenvalue is $\hbar$.

$$Y_l^m(\theta,\phi) = P_l^m(\cos\theta)\, e^{im\phi}$$

where $P_l^m(\cos\theta)$ is the associated Legendre function. For $l = 0$, $m = 0$, the spherical harmonic is just a constant, independent of θ and ϕ.

- Spherical harmonics are orthogonal to each other and form a complete set in (θ,ϕ) space. Any function of θ and ϕ may be written as a linear combination of spherical harmonics.
- Any three operator J_x, J_y, J_z satisfying the commutation relations

$$\left[J_x, J_y\right] = i\hbar\, J_z, \quad \left[J_y, J_z\right] = i\hbar\, J_x, \quad \left[J_z, J_x\right] = i\hbar\, J_y$$

are called angular momentum operators in quantum mechanics.

- The possible eigenvalues of $J^2 = J_x^2 + J_y^2 + J_z^2$ and J_z, allowed by the commutation relation, are $j(j+1)\hbar^2$ and $m\hbar$ where j can be any nonnegative integer or half integer and m can take any value from $-j$ to $+j$ in steps of 1.

Solved Problems

1. Simplify the commutators (a) $[P_x, L_x]$ and (b) $[P_x, L_y]$.

***Solution:* (a)** $$[P_x, L_x] = [P_x, YP_z - ZP_y] = [P_x, YP_z] - [P_x, ZP_y].$$

Any two of P_x, Y and P_z commute with each other. So any combination of these will commute with any other combination. So the first commutator $[P_x, YP_z] = 0$. Similarly, P_x, Z and P_y commute with each other. So the second commutator $[P_x, ZP_Y]$ is also zero. So, $[P_x, L_x] = 0$.

(b) $$[P_x, L_y] = [P_x, ZP_x - XP_z] = [P_x, ZP_x] - [P_x, XP_z].$$

The first commutator involves only two operators Z and P_x and they commute. Hence it is zero. The second commutator has P_x, X, P_z. As X and P_x do not commute, this commutator may not be zero.

$$[P_x, L_y] = -[P_x, XP_z] = -X[P_x, P_z] - [P_x, X]P_z = 0 + i\hbar\, P_z.$$

Thus $$[P_x, L_y] = i\hbar\, P_z.$$

2. Which of the following are eigenfunctions of L_z? For the cases where the function is an eigenfunction of L_z, find the corresponding eigenvalue.

(a) $\sin\theta e^{i\phi}$ (b) $e^{i(\theta+\phi)}$ (c) $e^{i\theta}\sin\phi$ (d) $r^n\cos\theta$

Solution: $L_z = -i\hbar\dfrac{\partial}{\partial\phi}$.

(a) $$-i\hbar\frac{\partial}{\partial\phi}\left(\sin\theta e^{i\phi}\right) = (-i\hbar)\sin\theta(i)e^{i\phi} = \hbar\sin\theta e^{i\phi}.$$

So $\sin\theta e^{i\phi}$ is an eigenfunction of L_z and the corresponding eigenvalue is $\hbar$.

(b) $$-i\hbar\frac{\partial}{\partial\phi}e^{i(\theta+\phi)}=(-i\hbar)(i)e^{i(\theta+\phi)}=\hbar e^{i(\theta+\phi)}.$$

So $e^{i(\theta+\phi)}$ is an eigenfunction of L_z and the corresponding eigenvalue is $\hbar$.

(c) $$-i\hbar\frac{\partial}{\partial\phi}\left(e^{i\theta}\sin\phi\right)=-i\hbar\, e^{i\theta}\cos\phi.$$

So $e^{i\theta}\sin\theta$ is not an eigenfunction of L_z

(d) $$-i\hbar\frac{\partial}{\partial\phi}\left(r^n\cos\theta\right)=0=0.\left(r^n\cos\theta\right)$$

So $r^n\cos\theta$ is an eigenfunction of L_z and the corresponding eigenvalue is zero.

3. (a) Is $\cos\theta+\sin\theta\, e^{i\phi}$ an eigenfunction of L^2? If yes, what is the corresponding eigenvalue?

(b) Is $\cos\theta+\sin\theta\, e^{i\phi}$ an eigenvalue of L_z? If yes, what is the corresponding eigenvalue?

Solution: (a) $Y_1^0(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\theta$ and $Y_1^1(\theta,\phi)=-\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}$.

Thus $\cos\theta+\sin\theta\, e^{i\phi}=c_1Y_1^0(\theta,\phi)+c_2Y_1^1(\theta,\phi)$ where c_1, c_2 are constant.

$$\begin{aligned}L^2\left(\cos\theta+\sin\theta\, e^{i\phi}\right)&=c_1L^2Y_1^0(\theta,\phi)+c_2L^2Y_1^1(\theta,\phi)\\&=c_1 2\hbar^2Y_1^0(\theta,\phi)+c_2 2\hbar^2Y_1^1(\theta,\phi)\\&=2\hbar^2\left[c_1Y_1^0(\theta,\phi)+c_2Y_1^1(\theta,\phi)\right]\\&=2\hbar^2\left[\cos\theta+\sin\theta\, e^{i\phi}\right].\end{aligned}$$

Thus, $\cos\theta+\sin\theta\, e^{i\phi}$ is an eigenfunction of L^2 and the corresponding eigenvalue is $2\hbar^2$.

(b) $$\begin{aligned}L_z\left(\cos\theta+\sin\theta\, e^{i\phi}\right)&=c_1L_zY_1^0(\theta,\phi)+c_2L_zY_1^1(\theta,\phi)\\&=c_1.0+c_2\hbar\, Y_1^1(\theta,\phi)\\&=\hbar\sin\theta\, e^{i\phi}.\end{aligned}$$

Thus, $\cos\theta+\sin\theta\, e^{i\phi}$ is not an eigenfunction of L_z.

4. It is given that $Y_2^0(\theta,\phi)=\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right)$. Applying L_+, find the expressions for $Y_2^1(\theta,\phi)$ and $Y_2^2(\theta,\phi)$.

Solution: Expressions for L_x and L_y are given in Equations 18.4 and 18.5 in terms of θ, ϕ. Using these,

$$L_+=L_x+iL_y=\hbar\, e^{i\phi}\left(\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\phi}\right).$$

You can write $Y_2^0(\theta,\phi)$ as $|2,0\rangle$ Also,

$$L_+|l\ m\rangle=\hbar\sqrt{(l-m)(l+m+1)}\ |l\ \ m+1\rangle\ .$$

Thus $$L_+|2,0\rangle=\hbar\sqrt{6}|2,1\rangle$$

or $$|2,1\rangle=\frac{1}{\hbar\sqrt{6}}L_+|2,0\rangle$$

or
$$Y_2^1(\theta,\phi) = \frac{1}{\hbar\sqrt{6}}\hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)Y_2^0(\theta,\phi)$$
$$= \frac{1}{\sqrt{6}}\sqrt{\frac{5}{16\pi}}\,e^{i\phi}\left[\frac{\partial}{\partial\theta}\left(3\cos^2\theta - 1\right) + i\cot\theta\frac{\partial}{\partial\phi}\left(3\cos^2\theta - 1\right)\right]$$
$$= -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{i\phi}.$$

Operate L_+ on $Y_2^1(\theta,\phi)$
$$L_+|2,1\rangle = \hbar\sqrt{(2-1)(2+1+1)}\,|2,2\rangle$$
$$|2,2\rangle = \frac{1}{2\hbar}L_+|2,1\rangle$$
$$= \frac{1}{2\hbar}\hbar\, e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)\left(-\sqrt{\frac{15}{8\pi}}\right)\left(\sin\theta\cos\theta\, e^{i\phi}\right)$$
$$= \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\phi}.$$

5. The operator associated with the measurement of the product $l_x l_y$ is $(L_xL_y + L_yL_x)/2$. Calculate the mean value of $l_x l_y$ in the state $|l\,m\rangle$.

Solution: We have $L_+ = L_x + iL_y$ and $L_- = L_x - iL_y$.

So,
$$L_x = \frac{L_+ + L_-}{2},\quad L_y = \frac{L_+ - L_-}{2i}.$$

Thus,
$$L_xL_y = \frac{(L_+ + L_-)(L_+ - L_-)}{4i}$$
$$= \frac{L_+^2 - L_-^2 - L_+L_- + L_-L_+}{4i}$$

and
$$L_yL_x = \frac{(L_+ - L_-)(L_+ + L_-)}{4i}$$
$$= \frac{L_+^2 - L_-^2 + L_+L_- - L_-L_+}{4i}.$$

So
$$L_xL_y + L_yL_x = \frac{L_+^2 - L_-^2}{2i}.$$

The mean value of $l_x l_y$ is equal to
$$\left\langle l\,m\left|\frac{L_xL_y + L_yL_x}{2}\right|l\,m\right\rangle = \frac{1}{4i}\left[\left\langle l\,m\left|L_+^2\right|l\,m\right\rangle - \left\langle l\,m\left|L_-^2\right|l\,m\right\rangle\right].$$

Now $L_+|l\,m\rangle$ gives a wave function proportional to $|l\;\;m+1\rangle$. Applying L_+ on this state will give a wave function proportional to $|l\;\;m+2\rangle$. So,
$$L_+^2|l\,m\rangle = c|l\;\;m+2\rangle$$

giving
$$\left\langle l\,m\left|L_+^2\right|l\,m\right\rangle = c\langle l\,m|l\;\;m+2\rangle = 0$$

as the eigenfunctions of L_z corresponding to different eigenvalues $m\hbar$ and $(m+2)\hbar$ are orthogonal to each other.

Similarly, $L_-^2|l\,m\rangle = c|l\,m-2\rangle$

giving $\langle l\,m|L_-^2|l\,m\rangle = c\langle l\,m|l\;m-2\rangle = 0$.

Hence the mean value of $L_x L_y$ is zero.

6. Find $\langle L_+\rangle$ in the state $\frac{1}{\sqrt{3}}\left[|11\rangle + |10\rangle + |1-1\rangle\right]$ where the first number in each term represents l and the second term represents m.

Solution:

$$\langle L_+\rangle = \frac{1}{3}\Big[\langle 11|L_+|11\rangle + \langle 11|L_+|10\rangle + \langle 11|L_+|1-1\rangle + \langle 10|L_+|11\rangle + \langle 10|L_+|10\rangle + \langle 10|L_+|1-1\rangle$$

$$+ \langle 1-1|L_+|11\rangle + \langle 1-1|L_+|10\rangle + \langle 1-1|L_+|1-1\rangle\Big].$$

L_+ will raise the value of m to $m+1$. Only those terms will survive in which this raised value of m in the ket is equal to the value of m in the bra. Thus,

$$\langle L_+\rangle = \frac{1}{3}\left[\langle 11|L_+|10\rangle + \langle 10|L_+|1-1\rangle\right]$$

$$= \frac{1}{3}\left[\langle 11|\sqrt{2}\hbar|11\rangle + \langle 10|\sqrt{2}\hbar|10\rangle\right] = \frac{2\sqrt{2}\hbar}{3}.$$

7. Show that if $J_-|j\,m\rangle = 0$, m must be equal to $-j$

Solution: We have,

$$J_-|j\,m\rangle = \hbar\sqrt{(j+m)(j-m+1)}\,|j\;m-1\rangle.$$

If this is zero, either $j+m=0$ giving $m=-j$, or $j-m+1=0$ giving $m=j+1$. But m cannot be $j+1$ so $m=-j$.

EXERCISES

1. Simplify the commutator $[P_x, L_z]$. **Ans.** $-i\hbar P_y$
2. Simplify the commutators $[X, L_x]$, $[Y, L_x]$ and $[Z, L_x]$. **Ans.** $0, -i\hbar Z, i\hbar Y$
3. Show that $\left[J^2, J_x\right] = 0$.
4. Find the expectation value of J_x^2 in the state $|jm\rangle$. **Ans.** $\frac{\hbar^2}{2}\left[j(j+1)-m^2\right]$
5. Find $\langle L_x\rangle$ and $\langle L_y\rangle$ in the state $|\phi\rangle = \frac{1}{\sqrt{3}}\left[|11\rangle + |10\rangle + |1-1\rangle\right]$ where the first number in each in the square bracket denotes l and the second number denotes m. **Ans.** $\frac{2\sqrt{2}\hbar}{3}, 0$
6. What is Hermitian adjoint of J_+J_-? **Ans.** J_+J_-

7. Consider a function $f(\theta,\phi) = Y_1^1(\theta,\phi) + Y_2^0(\theta,\phi)$. Find $L^2 f(\theta,\phi)$ and $L_z f(\theta,\phi)$.

Ans. $2\hbar^2\left(Y_1^1(\theta,\phi) + 3Y_2^0(\theta,\phi)\right), \hbar Y_1^1(\theta,\phi)$

8. Using the expressions of L_x and L_y given in the text, obtain the relations

$$L_+ = \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right) \text{ and } L_- = \hbar e^{-i\phi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$$

9. Using explicit expressions in terms of θ, ϕ show that $L_+Y_1^1(\theta,\phi)$ and $L_-Y_1^{-1}(\theta,\phi)$ are zero.

10. The function $Y_l^l(\theta,\phi)$ may be written as $f(\theta)e^{il\phi}$. Using the explicit expression of L_+ and the result that $L_+Y_l^l(\theta,\phi) = 0$, find the functional form of $f(\theta)$.

Ans. $(\sin\theta)^l$

11. Suppose $|l\ m\rangle$ is a unique eigenfunction of L^2 and L_z in the (θ,ϕ) space with eigenvalue $l(l+1)\hbar^2$ of L^2 and $m\hbar$ of L_z. Show that $|l\ \ m+1\rangle$ is also a unique eigenfunction of L^2 and L_z in this space with eigenvalues $l(l+1)\hbar^2$ of L^2 and $(m+1)\hbar$ of L_z.

12. In a simple model of rotating diatomic molecule, the Hamiltonian is given by $H = L^2/(2\mu r^2)$ where L^2 is the angular momentum square operator, μ is the reduced mass of the molecule and r is the separation between the atoms. (a) Find the quantized energy eigenvalues. (b) Assume that the transitions take place only between neighbouring energy levels. Show that the frequencies of the emitted radiation are equispaced.

Ans. $E_l = l(l+1)\dfrac{\hbar^2}{2\mu r^2}, \quad l = 0, 1, 2, \ldots$

19

The Spinning Electron — Spin Angular Momentum

I have shown in the previous chapter that the square of the angular momentum $\mathbf{r} \times \mathbf{p}$ of a particle can have values $l(l+1)\hbar^2$ where l is any nonnegative integer. Thus the allowed values are 0, $2\hbar^2$, $6\hbar^2$, $12\hbar^2$, etc. On the other hand if I don't use the expression $\mathbf{r} \times \mathbf{p}$ and use only the commutation relations between the angular momentum operators, the allowed values for the square of the angular momentum are $j(j+1)\hbar^2$ where j can be a nonnegative integer or a nonnegative half integer. So, apart from the values 0, $2\hbar^2$, $6\hbar^2$, etc., it can also have values like $3\hbar^2/4$, $15\hbar^2/4$, etc. The question is whether a particle can have these values of angular momentum square or these are coming only due to mathematical properties of commutation relations.

The answer to this question is that all electrons, all protons and all neutrons, that is, all of our most familiar building blocks of matter have angular momenta corresponding to half integral quantum numbers and not integral quantum numbers. Thus the angular momentum square of an electron is $3\hbar^2/4$ or $15\hbar^2/4$ or $35\hbar^2/4$ etc., and never 0 or $2\hbar^2$ or $6\hbar^2$ etc. But any kind of motion of an electron that you can think of, will only give it angular momentum square equal to 0 or $2\hbar^2$ or $6\hbar^2$ etc., and never $3\hbar^2/4$ as any motion corresponds to angular momentum $\mathbf{r} \times \mathbf{p}$. If an electron is having angular momentum square $3\hbar^2/4$ it cannot be due to its motion but must be due to some other source. So there are two kinds of angular momenta of a particle, one due to its motion in space and the other due to some intrinsic properties of the particle. The first kind of angular momentum is called the *orbital angular momentum* and the second kind is called the *spin angular momentum*.

The spin angular momentum is generally denoted by the symbol s. Thus the spin angular momentum square is written as s^2 and the x-, y-, z- components as s_x, s_y, s_z. The eigenvalues of s^2 are written as $s(s+1)\hbar^2$ and that of s_z as $m_s\hbar$. An interesting property of the spin angular momentum of an elementary particle (like an electron) is that it always has a fixed value of s. For an electron $s = 1/2$. You measure the spin angular momentum square of an electron and you will get $3\hbar^2/4$ and nothing else. You measure the z-component of the spin angular momentum and you get $\hbar/2$ or $-\hbar/2$ and nothing else. This is true for all electrons in all kinds of motion. It can be an electron during its transit from the electron gun to the screen in a TV display or an electron in a hydrogen atom or a free electron of a metal or any thing else that you can imagine. The spin angular momentum is therefore also called intrinsic or built-in angular momentum. As $s = 1/2$ for an electron, it is called a *spin-half particle*. Protons and neutrons are also spin-half particles. By the word spin, you may get a picture of the electron as a ball-like object rotating about its diameter. Indeed you know that the earth spins about the line joining its north pole and south pole and the phenomenon of day-night in 24 hours results from that. In introductory treatments many teachers prefer to introduce spin angular momentum of particles in this fashion. Chemists often describe the two possibilities $s_z = \hbar/2$ and $-\hbar/2$ by saying that the electron can spin in clockwise direction or anticlockwise direction. However these types of description steal away the beauty of the spin angular momentum. I emphasize that you imagine *any kind of motion* of an electron and that will come under orbital angular momentum. The spin angular momentum has no classical analogue. How do we know that a particle has spin angular momentum, and if it has how do we measure it? It turns out that the particles have magnetic moment once they have angular momentum. We can measure the magnetic moment of the given particle and from that learn about its spin and orbital angular momentum.

19.1 Relation between magnetic moment and angular momentum

The basic source for producing a magnetic field, as told in a school physics course, is a current loop. A charged particle going in a circle with large velocities is equivalent to a current loop. Such a motion corresponds to a magnetic moment and an angular momentum. I will derive a relation between these two from this type of motion and hope that similar relation will hold for spin angular momentum also.

Fig. 19.1

Consider a particle of mass M and charge q, moving in a circle of radius r with a constant speed v (Figure 19.1). The time period of the motion is $T = 2\pi r/v$ and the frequency is $v/(2\pi r)$. So the particle crosses through any point on the circle $v/(2\pi r)$ times per unit time. Accordingly, a total charge of $qv/(2\pi r)$ goes through any point on the circle per unit time. So the equivalent current is

$$I = \frac{qv}{2\pi r}.$$

The magnetic moment due to this motion is

$$\mu = I\pi r^2 = \frac{qvr}{2} = \frac{q}{2M}(Mvr).$$

But Mvr is the angular momentum of the particle. Both the magnetic moment and the angular momentum are in the same direction (along the axis of the circle). You can therefore write

$$\boldsymbol{\mu} = \frac{q}{2M}\mathbf{l}$$

or,

$$\mu_z = \frac{q}{2M} l_z. \tag{19.1}$$

Thus the magnetic moment is proportional to the angular momentum.

You may be wondering how much faith I have in the classical physics methods. It turns out that although these types of calculations do not have a logical framework for direct transition to quantum mechanical results in general, but often give results quite close to the correct quantum mechanical relations. In the present case also, Equation 19.1 gives rigorously correct relation between the magnetic moment of a particle and its orbital angular momentum. For an electron $q = -e$ and the mass $M = m_e$. So,

$$\mu_z = -\left(\frac{e}{2m_e}\right) l_z. \tag{19.2}$$

If the particle is in an eigenstate of $\mathbf{L}_z$, the value of l_z is definite and is equal to the corresponding eigenvalue $m\hbar$. Don't confuse this m with the mass. I have used m_e for the mass of the electron and this m is the quantum number identifying the eigenvalue of $\mathbf{L}_z$. Thus

$$\mu_z = -\left(\frac{e\hbar}{2m_e}\right) m. \tag{19.3}$$

The quantity in parenthesis is a universal constant and is called *Bohr magneton*. The symbol μ_B is used to represent it. It is taken as the basic unit of magnetic moment in all studies of magnetism at micro level.

You see from Equation 19.1 that the magnetic moment of a particle is inversely proportional to its mass. Thus the magnetic moment of a proton will be 1836 times smaller than that of an electron. The neutron as such is an uncharged particle and you would not expect it to have magnetic moment. But it does show some magnetic moment but that is also very small. Thus the magnetic moment of an atom is almost exclusively due to its electrons and the contribution of nuclei is generally neglected.

You can see from Equation 19.3 that the magnetic moment in z-direction is proportional to m, the quantum number for the z-component of the angular momentum. Let us assume that this result is true for all kinds of angular momentum. This assumption is indeed true, the proportionality constant between μ and the angular momentum is different in different cases. If the angular momentum square is $j(j+1)\hbar^2$, the value of m may be anything from $-j$ to j in steps of one. So there are $(2j+1)$ discrete values. If j is an integer, $(2j+1)$ is an odd number and if j is half integer, $(2j+1)$ is an even number. Correspondingly μ_z can also take odd or even number of values. If an experiment can measure μ_z and we can count the number of values μ_z can have we have a chance to know whether j is an integer or a half integer. Stern-Gerlach experiment does just that.

19.2 Stern–Gerlach experiment

The idea

What happens if you put a short bar magnet in a magnetic field? The magnet rotates to align itself along the direction of the field. That is the principle of a compass needle which rotates itself to stay along the north–south direction. The magnetic field exerts a torque on the magnet. If the field is uniform there is no net force on the magnet so that the center does not accelerate and the magnet rotates about its center. But if the field is nonuniform, there is a net force on the magnet so that the magnet as a whole accelerates. If the field varies in the z-direction and the magnet has a magnetic moment μ_z in the z-direction, a force

$$F_z = \mu_z \frac{dB_z}{dz}$$

acts on it. Let us see how.

Suppose you have created a magnetic field whose z component B_z varies as a function of z (Fig. 19.2). Suppose B_z increases with z so that $\frac{dB_z}{dz}$ is positive. I place a bar magnet of pole strength m and length l in this field, the angle between the length of the magnet and the z-axis being θ.

The z-component of the force on the north pole is mB_2 and that on the south pole is mB_1 where B_2, B_1 are the values of B_z at the north pole and the south pole respectively. The net force on the magnet in the z-direction is

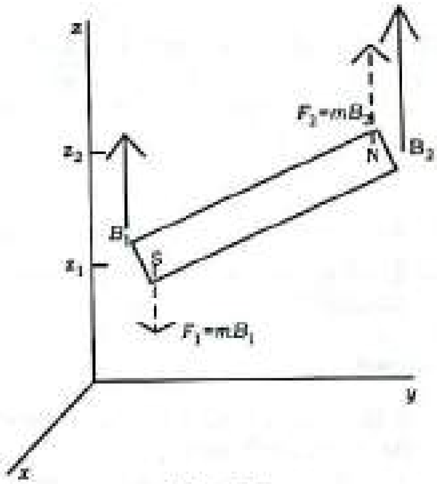

Fig. 19.2

$$F_z = m\left(B_2 - B_1\right) = \frac{\mu}{l}\left(B_2 - B_1\right)$$

where μ is the magnetic moment. Remember the magnetic moment, the pole strength m and the length l are related as $\mu = ml$.

You can write $F_z = \dfrac{\mu\left(B_2 - B_1\right)\cos\theta}{l\cos\theta} = \dfrac{\mu\cos\theta\left(B_2 - B_1\right)}{z_2 - z_1}$.

If the magnet is quite short, $\dfrac{B_2 - B_1}{z_2 - z_1} = \dfrac{dB_z}{dz}$. Also $\mu\cos\theta = \mu_z$.

So
$$F_z = \mu_z \frac{dB_z}{dz}. \tag{19.4}$$

I derived this expression using the magnetic pole picture. You get the same result if you start with a current loop which is a more realistic representation of a magnetic moment. The pole picture is mathematically equivalent to the current loop.

The idea of the Stern-Gerlach experiment is to create an inhomogeneous magnetic field in the z-direction and pass atoms through this field. The atoms will then deflect due to the force on them by the field and by measuring the deflection one can get information about μ_z.

The apparatus and the experiment

The main part of the apparatus is the magnet with specially designed pole pieces. Figure 19.3 shows the design schematically. The north pole is like a prism with a long edge facing a relatively flat south pole. Magnetic field lines are much more concentrated at the edge of the north pole and spread towards the south pole. A cross-sectional view of the field lines is also shown in Figure 19.3. Taking the z-axis as shown in the figure, there is a gradient of the magnetic field in the z-direction.

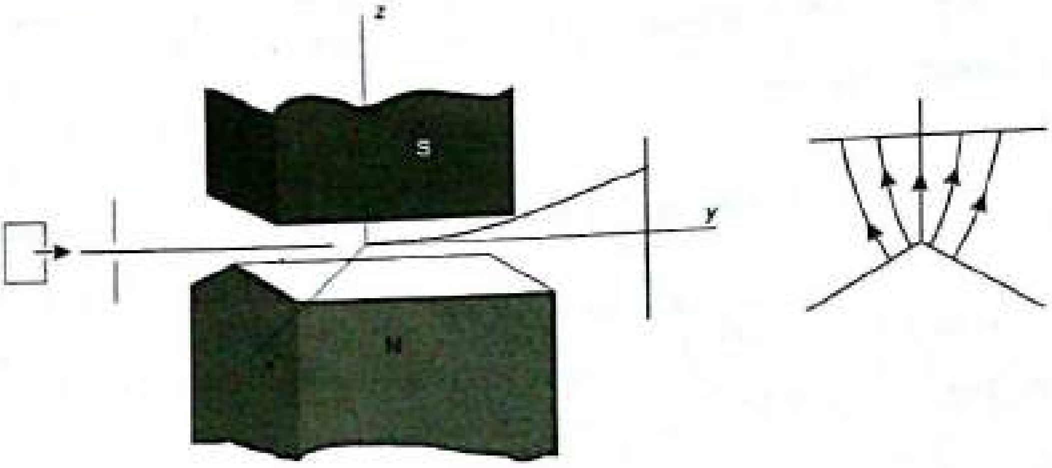

Fig. 19.3

Atoms of the desired element are sent in the space between the poles. For this, the material is heated in an oven to bring it in gaseous form. The atoms start out with some speed $(KE = 3kT/2)$ and enter the region between the pole pieces. Depending on the value of μ_z, a force acts on the atoms along the z-direction and turns their paths as long as they are inside that region. The atoms come out of the magnetic field and strike a receiving film where they leave permanent marks.

The result

The original experiment was performed by Stern and Gerlach in the year 1920 with silver atoms. A silver atom has 47 electrons, 46 of them pair up to give zero angular momentum and zero magnetic moment. The magnetic moment of a silver atom is then only due to the outermost single electron.

(a) (b)

Fig. 19.4

What do you expect if atoms followed rules of classical physics? Different atoms coming out of the oven will have different orientations in space but they all will have the same magnitude μ_0 of the magnetic moment. If the magnetic moment of a silver atom makes an angle θ with the z-axis, $\mu_z = \mu_0 \cos\theta$. As θ can take any value from 0 to π, μ_z will be continuously distributed between $-\mu_0$ and $+\mu_0$ when you consider a large number of atoms. As the force is proportional to μ_z, different atoms will be deflected by different angles and so there will be a continuous mark on the screen as shown in Figure 19.4a. The atoms which enter right under the edge of the north pole will deflect the largest and those entering at some distance away from this, will deflect less. That is why one expects an eye-type structure shown in Figure 19.4a.

And what do you expect from quantum mechanics? μ_z is proportional to the quantum number m which can only take discrete values from $-j$ to $+j$ if the angular momentum square of the silver atoms is $j(j+1)\hbar^2$. So μ_z can take only $(2j+1)$ discrete values and hence you expect $(2j+1)$ separate lines on the screen.

And what did Stern and Gerlach observe when they performed the experiment in 1920? The pattern on the screen was something like that shown in Figure 19.4b. The beam splits into two parts.

The discrete pattern confirms the quantum mechanical nature of angular momentum and magnetic moment. The fact that the beam splits into two parts show that μ_z and hence m can take only two values. Thus $2j + 1 = 2$ or $j = 1/2$. Thus, this experiment confirms the existence of half-integral values of the angular momentum quantum number and hence the existence of spin angular momentum. For silver atoms, the orbital angular momentum turns out to be zero in the ground state. The spin angular momentum square of the atom is $3\hbar^2/4$ corresponding $j = 1/2$. The z-component of the spin angular momentum is $\hbar/2$, or $-\hbar/2$ whatever way the silver atom is oriented. Thus μ_z has only two possible values, one positive and one negative and the beam splits into two parts.

The experiment has also been performed with hydrogen atoms, which are truly single electron atoms. The result is the same, the beam splits into two parts establishing the half integral angular momentum quantum number.

I have described this experiment and its results in a way to fit my introduction of spin angular moment. Historically the objectives of the experiments and the interpretation of the results were different.

19.3 The *g*-factor

The deflection of an atom in the Stern–Gerlach experiment is proportional to the z-component of the magnetic moment. Thus, from the deflection of the atoms one can calculate the value of μ_z. It is found that the value of μ_z for a single electron (a silver atom in ground state is equivalent to a single electron as far as μ_z is concerned) is very close to one Bohr magneton.

$$|\mu_{sz}| = \frac{e\hbar}{2m_e}. \tag{i}$$

I have put the subscript s in μ_{sz} to remind that this magnetic moment corresponds to the spin angular momentum. The value of the z-component of the angular momentum is $s_z = +\hbar/2$ or $s_z = -\hbar/2$. Taking direction into account, (i) can be written as

$$\mu_{sz} = -2\left(\frac{e}{2m_e}\right)s_z = -2\left(\frac{\mu_B}{\hbar}\right)s_z. \tag{19.5}$$

Equation 19.2 is

$$\mu_{lz} = -\left(\frac{e}{2m_e}\right)l_z = -\left(\frac{\mu_B}{\hbar}\right)l_z \tag{19.6}$$

where I have put an extra l in the subscript of μ_{lz} to remind that this magnetic moment corresponds to the orbital angular momentum. We write the above two equations in a combined form

$$\mu_z = -g\left(\frac{e}{2m_e}\right)j_z = -g\left(\frac{\mu_B}{\hbar}\right)j_z \tag{19.7}$$

where $g = 1$ for orbital angular momentum and 2 for spin angular momentum. The constant g is called the *g*-factor. The value 2 for spin angular momentum comes out from the experiment. The relativistic quantum theory developed by Dirac gives a slightly higher value of g.

μ_{lz} and μ_{sz} are the z-components of magnetic moment corresponding to orbital and spin angular momentum respectively. The z-component of the total magnetic moment is

$$\mu_z = \mu_{lz} + \mu_{sz}.$$

19.4 The spin wave functions and operators

The z-component of spin angular momentum of a particle is a physically measurable quantity and hence there must be a Hermitian operator corresponding to it. This operator is denoted as S_z. And if there is an operator S_z for the z-direction, there should also be operators S_x and S_y for x- and y-directions. These three operators satisfy the usual commutation relation for angular momentum, i.e., $[S_x, S_y] = i\hbar S_z, [S_y, S_z] = i\hbar S_x, [S_z, S_x] = i\hbar S_y$. The operator S^2 is defined as $S^2 = S_x^2 + S_y^2 + S_z^2$. The eigenvalues of S^2 are written as $s(s+1)\hbar^2$ and of S_z as $m_s\hbar$. The number s is called *spin angular momentum quantum number*. The quantum number m_s can take values from $-s$ to $+s$ in steps of 1. For electrons, s has just one value $s = 1/2$. Any electron in the universe has the same value of spin angular momentum quantum number. Choose any z-axis and measure the z-component of the spin angular momentum. It will be either $s_z = +\hbar/2$ ($m_s = +1/2$) or $-\hbar/2$ ($m_s = -1/2$). Even if you tilt the axes, s_z with the new direction will also be either $+\hbar/2$ or $-\hbar/2$. Similar is the case with protons and neutrons. The square of the spin angular momentum is $3\hbar^2/4$.

There are several elementary entities in an atom or a molecule or a nucleus. For example, in a helium nucleus there are two protons and two neutrons. In a hydrogen atom there is one proton and one electron. In a sliver atom there are 47 electrons apart from protons and neutrons. Each of these elementary entities has a spin angular momentum and possibly orbital angular momentum. The net angular momentum of such a composite particle is obtained by summing up all these angular momenta. However the addition of angular momenta involves sophisticated procedure and I will not tell you those in this book. But angular momenta of the elementary entities do tend to pair up to give a zero net value. The net angular momentum of the given particle is only due to a small number of unpaired elementary entities. For example, the net angular momentum of a nucleus in the ground state with even number of protons and even number of neutrons is always zero.

How do I write the expressions for the spin angular momentum operators S^2, S_x, S_y, S_z of an electron? You do not expect these expressions to be written in terms of x, y, z or r, θ, ϕ etc. Spin angular momentum has nothing to do with the space coordinates. It is in no way related to the motion of the electron is space. But still it recognizes the space directions. You set up a magnetic field in the z-direction and the spins (and hence the corresponding magnetic moments) are aligned accordingly. The measured values of S_z are $s_z = +\hbar/2$ and $-\hbar/2$. People give different symbols to describe these states. In one common use, these states are written as $\chi_{1/2}$ and $\chi_{-1/2}$. They are also called *spin-up* and *spin-down* states. Thus

$$S^2\chi_{1/2} = \frac{3}{4}\hbar^2\chi_{1/2}, \quad S_z\chi_{1/2} = \frac{\hbar}{2}\chi_{1/2}$$
$$S^2\chi_{-1/2} = \frac{3}{4}\hbar^2\chi_{-1/2}, \quad S_z\chi_{-1/2} = -\frac{\hbar}{2}\chi_{-1/2}.$$

Other common symbols are χ_+ and χ_-, and, $|\uparrow\rangle$ and $|\downarrow\rangle$.

$\chi_{1/2}$ and $\chi_{-1/2}$ are not the only possible spin states of an electron. It can also be a linear combination of these two such as $\chi = c_1\chi_{1/2} + c_2\chi_{-1/2}$. In this case, s_z does not have a definite value. If a measurement of s_z is made while the electron is in the state χ, you can get $\hbar/2$ with a probability $|c_1|^2$ and $-\hbar/2$ with a probability $|c_2|^2$. I have assumed that $|c_1|^2 + |c_2|^2 = 1$.

The wave function of an electron should contain all the information about the electron that it is possible to have. A wave function like $\psi(r, \theta, \phi)$ gives information about only the space related part. But the spin state should also come from the wave function. So, the total wave function of an electron (or any particle) is written as $\psi(r, \theta, \phi)\chi$ or a linear combination of terms like this. The space operators operate on the space part of the wave function and the spin operators operate on the spin part.

Any operator written in terms of space coordinates will commute with the spin operators. Thus all components of **L** will commute with all components of **S**. The eigenfunctions of S^2 and S_z are $f(r,\theta,\phi)\chi_{1/2}$ and $f(r,\theta,\phi)\chi_{-1/2}$ where $f(r,\theta,\phi)$ is an arbitrary function of r,θ,ϕ.

We talk of a separate spin space. For an electron or any spin-half particle, the spin space is 2-dimensional. This space can be described by two basis spin wave functions which we choose as $\chi_{1/2}$ and $\chi_{-1/2}$. All other spin wave functions are written as linear combinations of these two. Operation of S^2 and S_z on any wave function can then be easily written even though we do not have an explicit representation for either spin wave functions or for spin operators. But how do I operate S_x or S_y on a given spin wave function? Here is the procedure.

19.4.1 The raising and the lowering operators

As the spin operators S_x, S_y, S_z satisfy the commutation relations of an angular momentum, you can use all results derived for the general angular momentum in the previous chapter for spin angular momentum. Write

$$S_+ = S_x + iS_y, \quad S_- = S_x - iS_y. \tag{19.8}$$

These are raising and lowering operators respectively. You remember the results

$$J_+|j\ m\rangle = \sqrt{(j-m)(j+m+1)}\,\hbar|j\ \ m+1\rangle$$

and

$$J_-|j\ m\rangle = \sqrt{(j+m)(j-m+1)}\,\hbar|j\ \ m-1\rangle$$

where $|j\ m\rangle$ is the common eigenfunction of J^2 and J_z with eigenvalues $j(j+1)\hbar^2$ and $m\hbar$ respectively. If I write the spin wave functions as $|s,m_s\rangle$, the basis functions can be written as $\chi_{1/2} = \left|\frac{1}{2},\frac{1}{2}\right\rangle$ and $\chi_{-1/2} = \left|\frac{1}{2},-\frac{1}{2}\right\rangle$. Then,

$$S_+\chi_{1/2} = S_+\left|\frac{1}{2},\frac{1}{2}\right\rangle = 0$$

$$S_+\chi_{-1/2} = S_+\left|\frac{1}{2},-\frac{1}{2}\right\rangle = \sqrt{\left(\frac{1}{2}+\frac{1}{2}\right)\left(\frac{1}{2}-\frac{1}{2}+1\right)}\ \hbar\left|\frac{1}{2},\frac{1}{2}\right\rangle = \hbar\chi_{1/2}$$

$$S_-\chi_{1/2} = S_-\left|\frac{1}{2},\frac{1}{2}\right\rangle = \sqrt{\left(\frac{1}{2}+\frac{1}{2}\right)\left(\frac{1}{2}-\frac{1}{2}+1\right)}\ \hbar\left|\frac{1}{2},-\frac{1}{2}\right\rangle = \hbar\chi_{-1/2}$$

$$S_-\chi_{-1/2} = S_-\left|\frac{1}{2},-\frac{1}{2}\right\rangle = 0.$$

So now you can operate S_+ and S_- on any spin wave function. Write the operators S_x and S_y terms of S_+ and S_- as

$$S_x = \frac{S_+ + S_-}{2}, \qquad S_y = \frac{S_+ - S_-}{2i}$$

and you know how to operate these on any given spin wave function.

19.5 The matrix representation of spin wave functions and operators

A general spin wave function for a spin-$\frac{1}{2}$ particle can be written as $\chi = \alpha\,\chi_{1/2} + \beta\,\chi_{-1/2}$. Once you give me α and β, I know which spin wave function you are talking of. In other words, the spin wave function is completely specified by giving α and β. A general practice is to represent the wave function χ as a column matrix $\chi = \begin{bmatrix}\alpha\\ \beta\end{bmatrix}$. The basis functions are $\chi_{1/2} = \begin{bmatrix}1\\ 0\end{bmatrix}$ and $\chi_{-1/2} = \begin{bmatrix}0\\ 1\end{bmatrix}$.

Now suppose there is an operator S. Operate it on a general spin wave function $\chi = \alpha\,\chi_{1/2} + \beta\,\chi_{-1/2}$.

$$\mathrm{S}\,\chi = \alpha\,\mathrm{S}\,\chi_{1/2} + \beta\,\mathrm{S}\,\chi_{-1/2} = \chi'.$$

I wish to write this function as a linear combination of $\chi_{1/2}$ and $\chi_{-1/2}$. Let it be $\chi' = c_1\chi_{1/2} + c_2\chi_{-1/2}$. In matrix notation $\chi' = \begin{bmatrix}c_1\\ c_2\end{bmatrix}$.

What are c_1 and c_2? Take scalar product of χ' with $\chi_{1/2}$ to get c_1 and with $\chi_{-1/2}$ to get c_2.

$$c_1 = \langle\chi_{1/2}|\chi'\rangle = \langle\chi_{1/2}|\alpha\,\mathrm{S}\,\chi_{1/2} + \beta\,\mathrm{S}\chi_{-1/2}\rangle$$
$$= \alpha\langle\chi_{1/2}|\mathrm{S}|\chi_{1/2}\rangle + \beta\langle\chi_{1/2}|\mathrm{S}|\chi_{-1/2}\rangle$$

and

$$c_2 = \langle\chi_{-1/2}|\chi'\rangle = \langle\chi_{-1/2}|\alpha\,\mathrm{S}\,\chi_{1/2} + \beta\,\mathrm{S}\,\chi_{-1/2}\rangle$$
$$= \alpha\langle\chi_{-1/2}|\mathrm{S}|\chi_{1/2}\rangle + \beta\langle\chi_{-1/2}|\mathrm{S}|\chi_{-1/2}\rangle.$$

I can write χ' in matrix notation as

$$\chi' = \begin{bmatrix}\alpha\langle\chi_{1/2}|\mathrm{S}|\chi_{1/2}\rangle + \beta\langle\chi_{1/2}|\mathrm{S}|\chi_{-1/2}\rangle\\ \alpha\langle\chi_{-1/2}|\mathrm{S}|\chi_{1/2}\rangle + \beta\langle\chi_{-1/2}|\mathrm{S}|\chi_{-1/2}\rangle\end{bmatrix}$$
$$= \begin{bmatrix}\langle\chi_{1/2}|\mathrm{S}|\chi_{1/2}\rangle & \langle\chi_{1/2}|\mathrm{S}|\chi_{-1/2}\rangle\\ \langle\chi_{-1/2}|\mathrm{S}|\chi_{1/2}\rangle & \langle\chi_{-1/2}|\mathrm{S}|\chi_{-1/2}\rangle\end{bmatrix}\begin{bmatrix}\alpha\\ \beta\end{bmatrix}$$

where the usual matrix multiplication rule is used. So operating S on the spin wave function χ can be done by matrix methods as described below.

Write the 2×2 matrix

$$= \begin{bmatrix}\langle\chi_{1/2}|\mathrm{S}|\chi_{1/2}\rangle & \langle\chi_{1/2}|\mathrm{S}|\chi_{-1/2}\rangle\\ \langle\chi_{-1/2}|\mathrm{S}|\chi_{1/2}\rangle & \langle\chi_{-1/2}|\mathrm{S}|\chi_{-1/2}\rangle\end{bmatrix}.$$

This represents the operator S. Multiply this by the column matrix $\begin{bmatrix}\alpha\\ \beta\end{bmatrix}$, and you get the column matrix for $\mathrm{S}\chi$.

19.5.1 Matrices for some important spin operators

Matrix for S^2

$$\langle\chi_{1/2}|\mathrm{S}^2|\chi_{1/2}\rangle = \left\langle\chi_{1/2}\middle|\frac{3}{4}\hbar^2\chi_{1/2}\right\rangle = \frac{3}{4}\hbar^2\langle\chi_{1/2}|\chi_{1/2}\rangle = \frac{3}{4}\hbar^2$$

$$\langle \chi_{1/2}|S^2|\chi_{-1/2}\rangle = \langle \chi_{1/2}|\frac{3}{4}\hbar^2\, \chi_{-1/2}\rangle = \frac{3}{4}\hbar^2 \langle \chi_{1/2}|\chi_{-1/2}\rangle = 0$$

$$\langle \chi_{-1/2}|S^2|\chi_{1/2}\rangle = \langle \chi_{-1/2}|\frac{3}{4}\hbar^2\, \chi_{1/2}\rangle = \frac{3}{4}\hbar^2 \langle \chi_{-1/2}|\chi_{1/2}\rangle = 0$$

$$\langle \chi_{-1/2}|S^2|\chi_{-1/2}\rangle = \left\langle \chi_{-1/2}\left|\frac{3}{4}\hbar^2 \chi_{-1/2}\right.\right\rangle = \frac{3}{4}\hbar^2 \langle \chi_{-1/2}|\chi_{-1/2}\rangle = \frac{3}{4}\hbar^2.$$

So, the matrix for S^2 is $\left[S^2\right] = \begin{bmatrix} \frac{3}{4}\hbar^2 & 0 \\ 0 & \frac{3}{4}\hbar^2 \end{bmatrix} = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$

Matrix for S_z

$$\langle \chi_{1/2}|S_z|\chi_{1/2}\rangle = \left\langle \chi_{1/2}\left|\frac{\hbar}{2}\chi_{1/2}\right.\right\rangle = \frac{\hbar}{2}\langle \chi_{1/2}|\chi_{1/2}\rangle = \frac{\hbar}{2}$$

$$\langle \chi_{1/2}|S_z|\chi_{-1/2}\rangle = \langle \chi_{1/2}|-\frac{\hbar}{2}\chi_{-1/2}\rangle = -\frac{\hbar}{2}\langle \chi_{1/2}|\chi_{-1/2}\rangle = 0$$

$$\langle \chi_{-1/2}|S_z|\chi_{1/2}\rangle = \langle \chi_{-1/2}|\frac{\hbar}{2}\chi_{1/2}\rangle = \frac{\hbar}{2}\langle \chi_{-1/2}|\chi_{1/2}\rangle = 0$$

$$\langle \chi_{-1/2}|S_z|\chi_{-1/2}\rangle = \left\langle \chi_{-1/2}\left|-\frac{\hbar}{2}\chi_{-1/2}\right.\right\rangle = -\frac{\hbar}{2}\langle \chi_{-1/2}|\chi_{-1/2}\rangle = -\frac{\hbar}{2}.$$

So the matrix for S_z is $[S_z] = \begin{bmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$

Matrix for S_+

$$\langle \chi_{1/2}|S_+|\chi_{1/2}\rangle = 0$$
$$\langle \chi_{1/2}|S_+|\chi_{-1/2}\rangle = \langle \chi_{1/2}|\hbar|\chi_{1/2}\rangle = \hbar$$
$$\langle \chi_{-1/2}|S_+|\chi_{1/2}\rangle = 0$$
$$\langle \chi_{-1/2}|S_+|\chi_{-1/2}\rangle = \langle \chi_{-1/2}|\hbar|\chi_{1/2}\rangle = 0.$$

So, the matrix for S_+ is $[S_+] = \begin{bmatrix} 0 & \hbar \\ 0 & 0 \end{bmatrix} = \hbar\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}.$

Matrix for S_-

$$\langle \chi_{1/2}|S_-|\chi_{1/2}\rangle = \langle \chi_{1/2}|\hbar|\chi_{-1/2}\rangle = 0$$
$$\langle \chi_{1/2}|S_-|\chi_{-1/2}\rangle = 0$$

$$\langle \chi_{-1/2} | S_- | \chi_{1/2} \rangle = \langle \chi_{-1/2} | \hbar | \chi_{-1/2} \rangle = \hbar$$

$$\langle \chi_{-1/2} | S_- | \chi_{-1/2} \rangle = 0 .$$

So, the matrix for S_- is $[S_-] = \begin{bmatrix} 0 & 0 \\ \hbar & 0 \end{bmatrix} = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$.

Matrix for S_x

$$S_x = \frac{S_x + S_-}{2} .$$

So, $$[S_x] = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} .$$

Matrix for S_y

$$S_y = \frac{S_+ - S_-}{2i} = \frac{\hbar}{2i} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} .$$

19.6 Pauli spin operators and matrices

Pauli spin operators σ_x, σ_y and σ_z are defined by the relations

$$S_x = \frac{\hbar}{2}\sigma_x,\ S_y = \frac{\hbar}{2}\sigma_y \text{ and } S_z = \frac{\hbar}{2}\sigma_z . \tag{19.9}$$

The matrices for $\sigma_x, \sigma_y, \sigma_z$ are therefore,

$$[\sigma_x] = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix},\ [\sigma_y] = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \text{ and } [\sigma_z] = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} .$$

These are called Pauli spin matrices.

19.7 You learned in this chapter

- A particle can have two types of angular momentum, orbital angular momentum and spin angular momentum.
- Spin angular momentum is intrinsic to the particle and has no relation with the motion of the particle.
- The spin angular momentum operators of a particle are denoted by S^2, S_x, S_y, S_z. The eigenvalues of S^2 are $s(s+1)\hbar^2$ and of S_z are $m_s\hbar$.
- For all electrons $s = 1/2$ and m_s can be either $+1/2$ or $-1/2$.
- For protons and neutrons also, $s = 1/2$.
- The quantity $e\hbar/(2m_e)$ is called Bohr magneton and is used as a unit of magnetic moment.
- The magnetic moment of an electron is related to its angular momentum.

$$\mu_{lz} = -\left(\frac{\mu_B}{\hbar}\right) l_z, \quad \mu_{sz} = -2\left(\frac{\mu_B}{\hbar}\right) s_z .$$

- The spin state (corresponding to a definite spin) of an electron is represented by $\chi_{1/2}$ or $\chi_{-1/2}$ corresponding to $m_s = +1/2$ and $-1/2$. The complete wave function has a space part and a spin part. While the space part is written in terms of the space coordinates, the spin part is written in terms of $\chi_{1/2}$ and $\chi_{-1/2}$.
- The spin operators S^2 and S_z have simultaneous eigenfunctions $\psi(r,\theta,\phi)\,\chi_{m_s}$ where $\psi(r,\theta,\phi)$ is an arbitrary function.

Solved Problems

1. Draw a diagram showing the spin angular momentum of an electron by a vector and its possible z-components along a chosen z-axis. What angles can the vector make with the z-axis?

Solution: The square of the magnitude of the spin angular momentum is $3\hbar^2/4$. So the arrow representing the spin angular momentum must have a length proportional to $\sqrt{3}\,\hbar/2$. The z-component can be $\hbar/2$ or $-\hbar/2$. So the projection of the vector on the z-axis should either be $\hbar/2$ or $-\hbar/2$. The two possibilities for the vector are shown in Figure 19.W1. The angle θ is given by

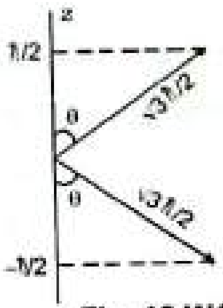

Fig. 19.W1

$$\cos\theta = \frac{\hbar/2}{\sqrt{3}\,\hbar/2} = \frac{1}{\sqrt{3}}$$

or,
$$\theta = \cos^{-1}\left(1/\sqrt{3}\right).$$

The angle with the z-axis can be $\cos^{-1}\left(1/\sqrt{3}\right)$ or $\pi - \cos^{-1}\left(1/\sqrt{3}\right)$.

2. The spin part of the wave function of an electron is $|\chi\rangle = \frac{1}{2}\left[\chi_{1/2} + \sqrt{3}\chi_{-1/2}\right]$. Calculate $S_x|\chi\rangle$, $S_y|\chi\rangle$ and $S_z|\chi\rangle$.

Solution:
$$S_x|\chi\rangle = \frac{1}{2}(S_+ + S_-)|\chi\rangle = \frac{1}{4}\left[S_+(\chi_{1/2} + \sqrt{3}\chi_{-1/2}) + S_-(\chi_{1/2} + \sqrt{3}\chi_{-1/2})\right]$$
$$= \frac{1}{4}\left[\sqrt{3}\hbar\chi_{1/2} + \hbar\chi_{-1/2}\right] = \frac{\hbar}{4}\left[\sqrt{3}\chi_{1/2} + \chi_{-1/2}\right].$$

Similarly,
$$S_y|\chi\rangle = \frac{1}{2i}(S_+ - S_-)|\chi\rangle = \frac{1}{4i}\left[S_+(\chi_{1/2} + \sqrt{3}\chi_{-1/2}) - S_-(\chi_{1/2} + \sqrt{3}\chi_{-1/2})\right]$$
$$= \frac{1}{4i}\left[\sqrt{3}\hbar\chi_{1/2} - \hbar\chi_{-1/2}\right] == \frac{\hbar}{4i}\left[\sqrt{3}\chi_{1/2} - \chi_{-1/2}\right].$$

And
$$S_z|\chi\rangle = \frac{1}{2}\left[S_z(\chi_{1/2}) + \sqrt{3}S_z(\chi_{-1/2})\right]$$
$$= \frac{1}{2}\left[\frac{\hbar}{2}\chi_{1/2} + \sqrt{3}\left(-\frac{\hbar}{2}\right)\chi_{-1/2}\right] = \frac{\hbar}{4}\left(\chi_{1/2} - \sqrt{3}\chi_{-1/2}\right).$$

3. The wave function of an electron at an instant is given by $\psi = f(r,\theta)e^{2i\phi}\chi_{1/2}$. Calculate the average value of the z-component of its magnetic moment.

Solution: The operator for the z-component of the magnetic moment is

$$\mu_z = \mu_{lz} + \mu_{sz} = \frac{\mu_B}{\hbar} L_z + 2\frac{\mu_B}{\hbar} S_z$$

The average value of μ_z in the given state is $\langle \mu_z \rangle = \langle \psi | \mu_z | \psi \rangle$

Now, $$\mu_z |\psi\rangle = \frac{\mu_B}{\hbar}\left[L_z|\psi\rangle + 2S_z|\psi\rangle\right] \tag{i}$$

The given wave function is $\psi = f(r,\theta)e^{2i\phi}\chi_{1/2}$. The ϕ dependent part is $e^{2i\phi}$. This shows that it is an eigenfunction of L_z with eigenvalue $2\hbar$. The spin dependent part is $\chi_{1/2}$. This shows that it is an eigenfunction of S_z with eigenvalue $+\hbar/2$. Thus

$$L_z|\psi\rangle = 2\hbar|\psi\rangle \text{ and } S_z|\psi\rangle = \frac{\hbar}{2}|\psi\rangle.$$

Using these in (i) $$\mu_z|\psi\rangle = \frac{\mu_B}{\hbar}\left[2\hbar|\psi\rangle + 2\frac{\hbar}{2}|\psi\rangle\right]$$

So, $$\langle\psi|\mu_z|\psi\rangle = \mu_B\left[2\langle\psi|\psi\rangle + \langle\psi|\psi\rangle\right] = 3\mu_B$$

4. Find the eigenvalues and the spin parts of the eigenfunctions of S_x for an electron.

Solution: Let the spin part of the eigenfunction of S_x be written as $\chi = \alpha\chi_{1/2} + \beta\chi_{-1/2}$ and the corresponding eigenvalue as λ. So $S_x\chi = \lambda\chi$.

$$\begin{aligned}
S_x\chi &= S_x\left[\alpha\chi_{1/2} + \beta\chi_{-1/2}\right] \\
&= \frac{1}{2}[S_+ + S_-]\left[\alpha\chi_{1/2} + \beta\chi_{-1/2}\right] \\
&= \frac{1}{2}\left[\alpha S_+(\chi_{1/2}) + \beta S_+(\chi_{-1/2}) + \alpha S_-(\chi_{1/2}) + \beta S_-(\chi_{-1/2})\right] \\
&= \frac{1}{2}\left[0 + \beta\hbar\chi_{1/2} + \alpha\hbar\chi_{-1/2} + 0\right] \\
&= \frac{\hbar}{2}\left[\beta\chi_{1/2} + \alpha\chi_{-1/2}\right]
\end{aligned}$$

Thus $$\frac{\hbar}{2}\left[\beta\chi_{1/2} + \alpha\chi_{-1/2}\right] = \lambda\left[\alpha\chi_{1/2} + \beta\chi_{-1/2}\right]$$

or $$\frac{\hbar\beta}{2} = \lambda\alpha \text{ and } \frac{\hbar\alpha}{2} = \lambda\beta \tag{i}$$

This gives $$\lambda^2 = \frac{\hbar^2}{4} \text{ or } \lambda = \pm\frac{\hbar}{2}$$

Using (i), $\lambda = \frac{\hbar}{2}$ gives $\alpha = \beta$, and $\lambda = -\frac{\hbar}{2}$ gives $\alpha = -\beta$.

Use the normalization condition $|\alpha|^2 + |\beta|^2 = 1$. For the first case $\alpha = 1/\sqrt{2}, \beta = 1/\sqrt{2}$ and for the second case $\alpha = 1/\sqrt{2}, \beta = -1/\sqrt{2}$. I have chosen real constants α and β. Thus the eigenvalues of S_x are $\pm\ \hbar/2$ and the corresponding eigenfunctions (spin part) are $\frac{1}{\sqrt{2}}\left(\chi_{1/2} \pm \chi_{-1/2}\right)$.

5. The spin part of the wave function of a spin-1/2 particle is $\cos\alpha\ \chi_{1/2} + \sin\alpha\ e^{i\beta}\chi_{-1/2}$. The x-component of the spin is measured. Find the probability of getting the result $\hbar/2$. Here α and β are real constants.

Solution: As deduced in the previous problem, the spin part of the eigenfunction of S_x corresponding to the eigenvalue $\hbar/2$ is $|\chi\rangle = \frac{1}{\sqrt{2}}(\chi_{1/2} + \chi_{-1/2})$. The wave function before the measurement is $|\chi_1\rangle = \cos\alpha\ \chi_{1/2} + \sin\alpha\ e^{i\beta}\chi_{-1/2}$. The probability of getting $\hbar/2$ in a measurement of S_x is $|\langle\chi_1|\chi\rangle|^2$.

$$\begin{aligned}\langle\chi_1|\chi\rangle &= \frac{1}{\sqrt{2}}\left\langle\cos\alpha\ \chi_{1/2} + \sin\alpha\ e^{i\beta}\chi_{-1/2}\middle|\chi_{1/2} + \chi_{-1/2}\right\rangle \\ &= \frac{1}{\sqrt{2}}\left[\cos\alpha\langle\chi_{1/2}|\chi_{1/2}\rangle + \sin\alpha\ e^{-i\beta}\langle\chi_{-1/2}|\chi_{-1/2}\rangle\right] \\ &= \frac{1}{\sqrt{2}}\left(\cos\alpha + \sin\alpha\ e^{-i\beta}\right)\end{aligned}$$

Thus the probability is

$$\begin{aligned}|\langle\chi_1|\chi\rangle|^2 &= \frac{1}{2}\left(\cos\alpha + \sin\alpha\ e^{-i\beta}\right)\left(\cos\alpha + \sin\alpha\ e^{i\beta}\right) \\ &= \frac{1}{2}[1 + 2\cos\alpha\sin\alpha\cos\beta]\end{aligned}$$

6. Find the eigenvalues and spin eigenstates of the operator $S_1 = S_x + S_y$.

Solution: I will use the matrices of S_x, S_y to solve the problem.

$$S_x = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} \text{ and } S_y = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}$$

So, $S_1 = S_x + S_y = \frac{\hbar}{2}\begin{bmatrix}0 & 1-i\\ 1+i & 0\end{bmatrix}$.

Let $\chi = \alpha\chi_{1/2} + \beta\chi_{-1/2}$ be an eigenfunction of S_1 with eigenvalue λ. Then,

$$S_1\chi = \lambda\chi.$$

In matrix notation, this becomes

$$\frac{\hbar}{2}\begin{bmatrix}0 & 1-i\\ 1+i & 0\end{bmatrix}\begin{bmatrix}\alpha\\ \beta\end{bmatrix} = \lambda\begin{bmatrix}\alpha\\ \beta\end{bmatrix}$$

or, $\frac{\hbar}{2}\begin{bmatrix}\beta(1-i)\\ \alpha(1+i)\end{bmatrix} = \lambda\begin{bmatrix}\alpha\\ \beta\end{bmatrix}$

or, $\frac{\hbar}{2}\beta(1-i) = \lambda\alpha$ (i)

and $\frac{\hbar}{2}\alpha(1+i) = \lambda\beta$. (ii)

Thus, $\frac{\hbar^2}{4}\alpha\beta(1-i)(1+i) = \lambda^2\alpha\beta$

or, $\lambda^2 = \frac{\hbar^2}{2}$ or $\lambda = \pm\frac{\hbar}{\sqrt{2}}$

Thus the eigenvalues are $\pm\hbar/\sqrt{2}$.

Putting $\lambda = +\frac{\hbar}{\sqrt{2}}$ in (i),

$$\frac{\hbar}{2}\beta(1-i) = \frac{\hbar}{\sqrt{2}}\alpha$$

or, $\beta = \frac{\sqrt{2}}{1-i}\alpha = \frac{1+i}{\sqrt{2}}\alpha$.

The eigenfunction corresponding to the eigenvalue $\hbar/\sqrt{2}$ is $\chi_1 = \alpha\left(\chi_{1/2} + \frac{1+i}{\sqrt{2}}\chi_{-1/2}\right)$.

The norm of this function is $|\alpha|^2\left[1+\frac{(1+i)(1-i)}{2}\right] = 2|\alpha|^2$. Taking $\alpha = \frac{1}{\sqrt{2}}$, the function χ_1 will be normalized. So I write the eigenfunction as $\chi_1 = \frac{1}{\sqrt{2}}\chi_{1/2} + \frac{1+i}{2}\chi_{-1/2}$.

Similarly a normalized eigenfunction corresponding to the eigenvalue $-\hbar/\sqrt{2}$ is, $\chi_2 = \frac{1}{\sqrt{2}}\chi_{1/2} - \frac{1+i}{2}\chi_{-1/2}$.

7. Calculate $(L_xS_x)\left[Y_1^0(\theta,\phi)\chi_{1/2}\right]$.

Solution: $(L_xS_x)\left[Y_1^0(\theta,\phi)\chi_{1/2}\right] = L_xY_1^0(\theta,\phi)S_x\chi_{1/2}$

Now
$$L_xY_1^0(\theta,\phi) = \left(\frac{L_+ + L_-}{2}\right)Y_1^0(\theta,\phi).$$
$$= \frac{1}{2}\left[L_+Y_1^0(\theta,\phi) + L_-Y_1^0(\theta,\phi)\right]$$
$$= \frac{1}{2}\left[\sqrt{2}\hbar\, Y_1^1(\theta,\phi) + \sqrt{2}\hbar\, Y_1^{-1}(\theta,\phi)\right]$$
$$= \frac{\hbar}{\sqrt{2}}\left[Y_1^1(\theta,\phi) + Y_1^{-1}(\theta,\phi)\right]$$

and
$$S_x\chi_{1/2} = \frac{S_+ + S_-}{2}\chi_{1/2} = \frac{\hbar}{2}\chi_{-1/2}.$$

Thus $(L_x S_x)\left[Y_1^0(\theta,\phi)\chi_{1/2}\right] = \frac{\hbar^2}{2\sqrt{2}}\left[Y_1^1(\theta,\phi) + Y_1^{-1}(\theta,\phi)\right]\chi_{-1/2}$.

EXERCISES

1. Which of the following nuclei will have integral value of angular momentum quantum number and which will have half integral values? ${}_2^3\text{He}, {}_2^4\text{He}, {}_7^{14}\text{N}, {}_{26}^{57}\text{Fe}, {}_{30}^{67}\text{Zn}$.

Ans. Integral: ${}_2^4\text{He}, {}_7^{14}\text{N}$; Half integral : ${}_2^3\text{He}, {}_{26}^{57}\text{Fe}, {}_{30}^{67}\text{Zn}$

2. A beam of identical particles sent in a Stern-Gerlach equipment splits in four parts. What is the maximum value of $m_l + m_s$ for these particles?

Ans. 3/2

3. Prove that the operator S_+^2 and S_-^2 are zero for the spin-1/2 space.

4. Show that $S_xS_y+S_yS_x=S_yS_z+S_zS_y=S_zS_x+S_xS_z=0$ for a spin-1/2 particle.

5. The wave function of an electron at a given time is $\psi=f(r)\left(-2\chi_{1/2}+3\chi_{-1/2}\right)$. Find the expectation value of the z-component of the magnetic moment of the electron at this time. **Ans.** $-5\mu_B/13$

6. Find the z-component of magnetic moment of an electron in the state $f(r,\theta)e^{i\phi}\chi_{-1/2}$. **Ans.** Zero

7. Find the value of g-factor for an electron in the state $f(r,\theta)e^{i\phi}\chi_{1/2}$. **Ans.** 4/3

8. An electron is in the state $l=0$, $m_s=1/2$ when the x-component of its magnetic moment is measured. What values may be obtained and with what probabilities? **Ans.** $\pm\mu_B$ with equal probability 0.5

9. Find the eigenvalues and spin parts of the eigenfunctions of S_y.

$$\textbf{Ans. } \frac{\hbar}{2},\left(\chi_{1/2}+i\chi_{-1/2}\right)/\sqrt{2};\ -\frac{\hbar}{2},\left(\chi_{1/2}-i\chi_{-1/2}\right)/\sqrt{2}$$

10. Let S' denote the component of S in the direction $\cos\theta\,\hat{j}+\sin\theta\,\hat{k}$ where $\hat{j}$ and $\hat{k}$ are unit vectors along the y and z axes. (a) Write the matrix of S' with basis states $\chi_{1/2}$ and $\chi_{-1/2}$. (b) Find the eigenvalues and eigenfunctions of S'.

$$\textbf{Ans. (a) } \frac{\hbar}{2}\begin{bmatrix}\sin\theta & -i\cos\theta\\ i\cos\theta & -\sin\theta\end{bmatrix},\ \text{(b) } \frac{\hbar}{2},-\frac{\hbar}{2},k\left(\chi_{1/2}+i\frac{1-\sin\theta}{\cos\theta}\chi_{-1/2}\right),k\left(\chi_{1/2}-i\frac{1+\sin\theta}{\cos\theta}\chi_{-1/2}\right)$$

11. Consider an atom with spin quantum number $s=1/2$. At a certain time the z-componant of the spin angular momentum is measured and is found to be $\hbar/2$. Immediately after this the component of spin angular momentum in the direction $\left(\sqrt{3}\,\hat{j}+\hat{k}\right)/2$ is measured. What is the probability that this component will be found to be $\hbar/2$? **Ans.** 0.75

12. Show that the Pauli spin matrices satisfy $\sigma_x\sigma_y\sigma_z=i$

13. Show that $\mathbf{L}\cdot\mathbf{S}=L_zS_z+\frac{1}{2}(L_+S_-+L_-S_+)$.

14. Calculate $\mathbf{L_x}\,\mathbf{S_x}\left[Y_1^0(\theta,\phi)\chi_{1/2}\right]$.

$$\textbf{Ans. } \frac{\hbar^2}{2\sqrt{2}}\left[(1+i)Y_1^1(\theta,\phi)+(1-i)Y_1^{-1}(\theta,\phi)\right]\chi_{-1/2}$$