Chapter 1
Introduction to Quantum Mechanics

1.1 Introduction

In Nanotechnology we are concerned with natural and synthetic materials in the size range of ∼1–100 nm. At such a small size, very familiar classical, Newtonian mechanics or thermodynamics are not able to explain the observed properties of materials. We have to use quantum mechanics sometimes directly and sometimes through subjects like solid state physics or chemistry which use it to explain the properties and phenomenon of different materials. Those of you who are familiar with quantum mechanics and solid state physics can skip this and the next chapter and directly go to the third chapter. For those who would like to start new, let us discuss first the need of quantum mechanics and how it got developed so that it can be used to understand atoms, molecules, solids and nanomaterials. Box 1.1 gives some historical milestones, which have led to quantum mechanics.

Box 1.1: Historical Milestones in the Development of Quantum Mechanics
Pre-quantum Era

- In 1669, Newton proposed that light had corpuscular or particle nature.
- Huygen claimed in 1690 that light had a wave nature.
- Kirchoff and others studied black body radiation around 1860.
- Maxwell proposed (1873) theory of electromagnetic waves.
- In 1803–04 Young performed double slit experiment, which showed that light had a wave nature.
- In 1887, Heinrich Hertz produced and detected electromagnetic radiation.

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Box 1.1 (continued)
Old Quantum Theory Period

- In 1901, Max Planck showed that energy distribution in black body radiation could be explained properly only if one considered that the radiation was quantized or had a particle nature.
- In 1905, Einstein proposed a theory of photoelectric effect which decisively proved that quantum or particle nature was associated with electromagnetic waves.
- Compton effect (1920) could be explained only when particle nature of electromagnetic radiation was considered, supporting Max Planck's and Einstein's theories. Particles of electromagnetic waves were identified as 'photons'.
- De Broglie (1923) argued that if electromagnetic waves were particles (photons) then why not particles have waves associated with them?
- Bohr's atom model (1913) with stationary states (why electrons should have some fixed energies) could be explained with de Broglie hypothesis.

Modern Quantum Theory Begins

- Heisenberg introduced (1925) Matrix Mechanics.
- Schrödinger equation (1926) gave the firm foundation for de Broglie hypothesis and later explained the electronic structure of atoms, molecules and solids.
- Davisson and Germer showed in 1927 that electrons can be diffracted. Regularly spaced atoms constitute multi-slit analogue of Young's double slit experiment.
- Heisenberg proposed uncertainty principle in 1928.

This marks the beginning of Quantum Mechanics as it is practiced now!

In Kirchoff's time many scientists were interested in understanding the black body radiation (Box 1.2). When any radiation is incident on a body, what will it do? It will either reflect (r), absorb (a) or transmit (t), though partially, so that $r + a + t = 1$. A material is called a 'black body' (see Box 1.3) if it absorbs all radiation incident on it without reflecting or transmitting it. When a black body is heated, it gives out a spectrum as shown in Fig. 1.1. The black body spectrum spreads over a large range of wavelengths and has a maximum in the intensity. Experiments on black body radiation led Stefan (1879) and Boltzman (1884) to establish Stefan-Boltzman law. According to this law, the total radiation from a

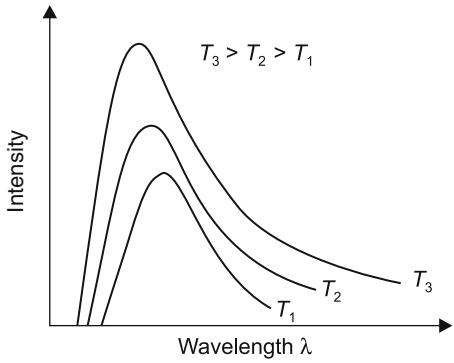

Fig. 1.1 Spectra of Black body radiation. Note that as the temperature increases, the spectral intensity increases and maximum intensity shifts to shorter wavelength. T_1, T_2 and T_3 are different temperatures in the increasing order

black body is proportional to the fourth power of absolute temperature. If E is the intensity of total radiation, and T the absolute temperature,

$$E = \sigma T^4 \tag{1.1}$$

where σ is known as Stefan's constant. Its value is $\sigma = 5.669 \times 10^{-8}$ W/m^2.

Later Wien showed that as the temperature of the black body increased, the maximum in the black body spectrum shifted to shorter wavelength or higher energy. To understand this, take a piece of charcoal or iron. At room temperature, they look black. If we heat these materials then what happens? First they look faint red, then they change to bright red and then become bright yellow or white. Wien's precise experiments on black body radiation resulted into a law which states that

$$\lambda_{max} \times T = \text{Wien displacement constant} \cong 2.898 \times 10^{-3} \text{ mK} \tag{1.2}$$

where λ_{max} is the wavelength at which maximum intensity occurs for a black body held at temperature T. He also tried to write an expression, which could show how the intensity varied with wavelength as

$$E_\lambda = \frac{a}{\lambda^5} \exp\left(\frac{-b}{\lambda T}\right) \tag{1.3}$$

where 'a' and 'b' are constants. $E_\lambda d\lambda$ is the rate of energy emission per unit area in the wavelength range λ to $\lambda + d\lambda$. Therefore total energy radiated per unit time, per unit surface area is given by

$$E = \int_0^\infty E_\lambda d\lambda \tag{1.4}$$

Box 1.2: Sir Isaac Newton (1643–1727)

Isaac Newton was born on 4th January 1643 in Woolsthrope, Lincolnshire, England. His father was a farmer who died two months before Isaac was born. His mother remarried and Newton had a difficult childhood. He graduated from Trinity College, Cambridge and studied Philosophy of Descartes, Gassendi, Hobbs and Boyle. He somewhere wrote, "Plato is my friend, Aristotle is my friend, but my best friend is truth". He also studied Kepler's optics and had a keen interest in mathematics. In 1665, he had to return home from college when an epidemic of plague broke.

In a period of 2 years at home, he did some revolutionary work in mathematics, physics and astronomy. He then laid the foundations of differential and integral calculus. He returned to college in 1667 and by 1669 he became well known due to his achievements in mathematics. In 1669, just at the age of 27, he was appointed as a Professor, Lucasian chair in Cambridge. His first lectures as a Professor were on Optics. All had believed since the time of Aristotle that white light was just a single component of radiation. But Newton's work during 2 years at home during plague, made him think otherwise. Newton became the Fellow of Royal Society in 1672. He left Cambridge and took a Government position as a Warden of Royal Mint in 1696 and Master in 1699. Newton took his job very seriously and contributed a lot to the work of Mint. Officially he left his Cambridge position in 1701. Newton was a real genius and worked in almost all areas important at that time but he is best known for his work in

Laws of Gravity
Optics and
Co-foundation of Calculus

His famous books are

Philosophiae Naturalis Principa Mathematica (1687) and Opticks (1704).
Philosophiae Naturalis Principa Mathematica, which is often referred to just as 'Principa', is considered to be one of the best scientific document ever written.

Newton was elected in 1703 as a President of Royal Society and remained so getting elected every year until his death on 31st March 1727 in London, England.

Box 1.3: Black Body Radiation
All materials absorb and emit energy. The intensity of energy radiated and absorbed by a body are equal if the object is in thermal equilibrium with its surrounding. However if the body is above the temperature of its surrounding then it emits radiation, which is known as black body radiation. Black body is thus an object that can absorb all radiation incident on it (no reflection or transmission!) or emits all radiation when above the temperature of the surrounding. Typical black body spectra are illustrated in Fig. 1.1.

Total intensity of radiation (area under the curve) and intensities at different emission wavelengths of a perfect black body irrespective of its material depend on the temperature. In practice a cavity with a small hole can act like a black body.

It was found that this formula holds good only for short wavelength side of the spectrum. Therefore scientists continued their efforts to find out a suitable equation which would be able to give or simulate the complete spectrum. Rayleigh and Jean arrived at an equation

$$E_\lambda = \frac{2c}{\lambda^4} kT \tag{1.5}$$

where 'c' is velocity of light and 'k' is Boltzman constant.

This equation could explain the long wavelength side of the black body spectrum. However it failed at short wavelengths. Thus none of the equations were satisfactory to explain the black body radiation over the entire range. The mystery continued until Planck proposed in 1901 a formula

$$E_\lambda = \frac{2\pi hc^2}{\lambda^5} \frac{1}{\left(e^{hc/\lambda KT} - 1\right)} \tag{1.6}$$

where h is Planck's constant. Planck proposed that radiation cannot be absorbed or emitted continuously. One needs to consider the absorption or emission of radiation through some quantum of energy or 'quanta' like particles, later termed as photons. Energy of each quantum of radiation (absorbed or emitted) was assumed to be $h\nu$, where ν is the frequency of absorbed or emitted radiation. It can be shown that above equation is valid at short and long wavelengths equally well. The total radiated energy is given by

$$E = \frac{2\pi^5 k^4}{15c^2h^3} T^4 \tag{1.7}$$

Thus Stefan's law follows from Planck's equation. Planck's equation can also be used to prove experimentally observed Wien's law. Planck's equation successfully explained all the regions of Black Body spectrum as well as previous findings and laws. Therefore Planck's idea that electromagnetic radiation should be considered as quantum of radiation turned out to be a milestone in the development of modern science (Box 1.4).

Box 1.4: Max Planck (1858–1947)

Max Planck was born in Kiel, Germany, in the year 1858. He studied physics in Munich as well as Berlin, Germany. He became a Professor of Theoretical Physics in 1892 in Berlin University. There he discovered in 1899 the fundamental constant '*h*' or Planck's constant named after him. Immediately in 1900 he discovered what is known now as 'Planck's law of black body radiation'.

This law became the foundation of quantum theory.

Max Planck was awarded the Nobel Prize for Physics in 1918. From 1930 to 1937, Planck was head of the Kaiser Wilhelm Gesellschaft zur Fördernen der Wissenschaften (KWG, Emperor Wilhelm Society for the Advancement of Science) which was renamed after his death on 4th October 1947 in Götingen, Germany as Max Planck Gesellschaft zur Förderung der Wissenschaften (MPG, Max Planck Society for the Advancement of Science). This institute continues to be one of the most important institutes for science in Germany.

Box 1.5: Photoelectric Effect

If two metal electrodes are placed in an evacuated tube, separated by a short distance, as illustrated in Fig. 1.2a then current flows in the circuit if cathode is irradiated with UV to visible light. This is known as photoelectric effect. It is easy to understand that the circuit is completed if electrons are emitted from cathode reaching the anode on illumination of the cathode. Einstein successfully explained in 1905 the observations by assuming that the incident beam of light behaved like photons or quanta of radiation proposed by Max Planck. His laws of photoelectricity are as follows:

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Box 1.5 (continued)

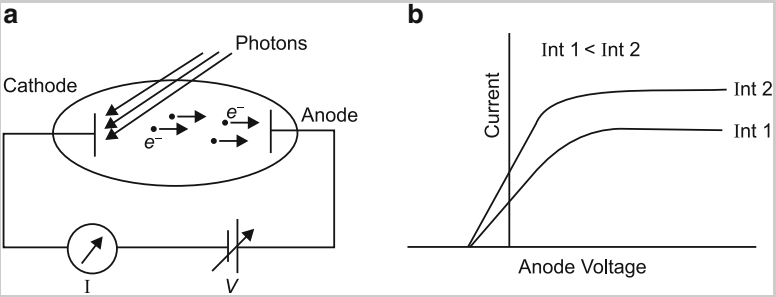

Fig. 1.2 (**a**) Circuit diagram to observe photoelectric effect. (**b**) Variation of current due to photoelectrons. Here 'Int' is the intensity of light

1. Photoelectric current (I) is proportional to the intensity of light (Int) falling on the cathode (see Fig. 1.2b).
2. There exists a threshold frequency dependent on the cathode material, which is necessary to emit photoelectrons. If light of lesser frequency is used then, even for any high intensity, no photoelectrons can be emitted.
3. This implies that there is a maximum kinetic energy which is necessary to produce photoelectric current.

$$k_{\max} = eV_0 = \frac{1}{2}mv^2 \tag{1.8}$$

where V_0 is the stopping potential, e and m are electron charge and mass respectively. The velocity is v.

Even if anode is negative (V_0), electrons with maximum kinetic energy eV_0 can reach the anode.

Maximum energy of emitted photoelectrons does not depend upon the intensity of incident light but the frequency used as illustrated in Fig. 1.3.

4. Emitted photoelectrons have maximum energy (corresponding to $-V_0$) which depends upon the frequency of incident light.

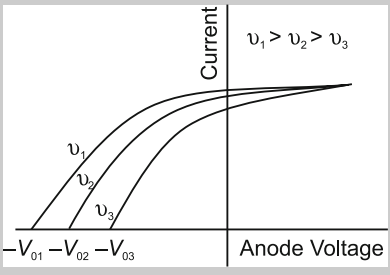

Fig. 1.3 Negative anode voltage V_0 denotes the maximum kinetic energy the electrons can have in a photoemission process. It depends on the frequency υ of the incident light

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Box 1.5 (continued)

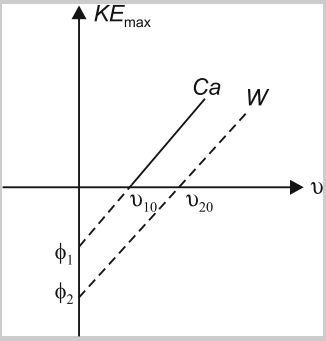

Fig. 1.4 Maximum kinetic energy depends upon the frequency of incident light and the material of cathode. Note that the lines have same slope (see Eq. 1.9). Here Ca and W are calcium and tungsten cathodes respectively. ϕ_1 and ϕ_2 are work functions of Ca and W respectively. Work function is a property of the material and denotes the amount of energy required to remove the electron from that material

Thus, number of ejected photoelectrons depends upon the intensity of light but the maximum kinetic energy of ejected photoelectrons depends upon the frequency of light. There is a minimum frequency 'υ_0' necessary to eject the photoelectrons which depends upon the material. This can be stated as

$$\text{Maximum kinetic energy} = h\upsilon - h\upsilon_0 \tag{1.9}$$

where $h\upsilon$ is the energy larger than minimum energy $h\upsilon_o$ required to eject the photoelectron (Fig. 1.4).

Box 1.6: Compton Scattering

X-rays with sufficiently high energy, when incident on a stationary electron as Compton imagined in 1920, can change their own direction as well as wavelength to longer side, reducing their energy. Reduced energy is imparted to the electron which gains a momentum $p = mv$ where m is the mass of the electron and v is the velocity gained by the electron.

$$\text{K.E of electron} = h\upsilon - h\upsilon' \tag{1.10}$$

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Box 1.6 (continued)
where υ and υ' are the frequencies of incident X-rays before and after scattering (Fig. 1.5).

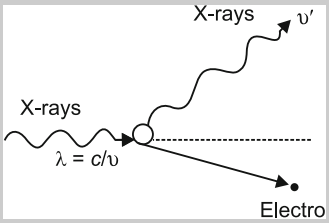

Fig. 1.5 Schematic of Compton effect $\upsilon' < \upsilon$

From conservation of momentum, momentum gained by the electron must be same as that lost by X-rays or we need to assume that X-rays which are electromagnetic waves have momentum $p = h/\lambda$ and X-rays behave as particles or photons.

Further, Einstein's theory of photoelectric effect (Box 1.5) and Compton effect (Box 1.6) could be explained only if one assumed the existence of photons or quanta of electromagnetic radiation.

However electromagnetic radiation also exhibits interference of light. This is quite evident from Young's diffraction experiments with single and double slits. It may, therefore, be concluded that it depends upon the type of experiment that electromagnetic radiation shows itself as waves or particles. Waves, of course, are continuous and particles are discrete in nature. The behaviour of electromagnetic waves sometimes as waves and sometimes as particles is termed as 'wave-particle duality' (Box 1.7).

Box 1.7: Albert Einstein (1879–1955)
Albert Einstein was born in Ulm, Germany, on 14th March 1879. At the age of four or five, his father showed him a compass and there begun his life long passion for physics. He wondered as a child how the mysterious force caused compass needle to move. He studied in a Catholic school in Munich, Germany. He was certainly not a top ranking student but he excelled in mathematics and physics. Even in school and college he was extremely original and independent in thinking.

He often challenged his teachers and the established scientific ideas. This perhaps resulted later into himself becoming a great scientist. At a very young age of 12, he studied geometry on his own and wrote his first scientific essay at the age of 16. He went to the University of Zurich for his college education and received Ph.D. there in 1905. In this year he wrote his four

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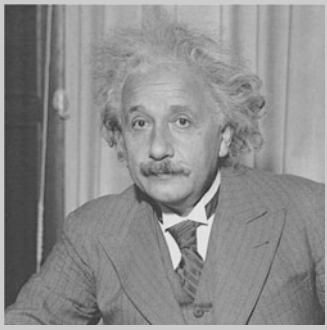
Box 1.7 (continued)
groundbreaking papers which were published in the journal 'Annalen der Physik'. These are as follows:

1. "On a Heuristic Point of View Concerning the Production and Transformation of Light"
   This deals with the photoelectric effect for which he received Nobel Prize in Physics in 1921.
2. "On the Movement of Small Particles Suspended in Stationary Liquids Required by the Molecular-Kinetic Theory of Heat"
3. "On the Electrodynamics of Moving Bodies"
   This paper is about his famous Theory of Relativity.
4. "Does the Inertia of a Body Depend upon its Energy Constant?"

$$\text{This paper has his famous equation } E = mc^2. \tag{1.11}$$



Interestingly, Einstein began his career as a Patent clerk at Swiss Federal Office for Intellectual Property in Bern. He spent 7 years there and was a guest lecturer for 1 year in the University of Bern. He then became the Professor of Theoretical Physics in the University of Zurich, Switzerland. Later he became a Swiss citizen. By 1909 he became very famous and visited many countries. In 1935 he went to U.S. and stayed there permanently in New Jersey. He was in the Institute of Advanced Studies in Princeton, New Jersey and made numerous scientific contributions. He also made until his death on 18th March 1955 numerous contributions to the world peace.

1.2 Matter Waves

It is quite logical to think that if electromagnetic waves sometimes behave like particles (photons) then why not particles behave like waves? This precisely was the point raised by de Broglie in 1923. He postulated that all the matter must have associated waves with wavelength given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} \tag{1.12}$$

where h = Planck's constant, p = magnitude of the momentum, m = mass of the particle and v = velocity of the particle.

Equation 1.12 is known as the de Broglie relation and wavelength l is known as de Broglie wavelength of the particle (Box 1.8).

Box 1.8: Louis de Broglie (1892–1987)

Louis de Broglie completed his school studies in Paris, France. He was interested in literary studies rather than science. He took a course in history at University of Paris as he wanted to make a career in diplomatic services. However he got interested in physics due to influence of his elder brother who was doing Ph.D. in experimental physics. So after getting a degree in Arts he enrolled himself for Ph.D. in physics.

However there broke the World War I and he had to serve in army. After 1920 he again returned to research in mathematical physics and was attracted by Planck's black body radiation and quantum theory concepts. In 1924 he put forth the particle-wave duality in his doctoral thesis for which he received the Nobel Prize for Physics in 1929. Some excerpt from his thesis which explains the background of his work is as follows.

> *Thirty years ago, physics was divided into two camps: ... the physics of matter, based on the concepts of particles and atoms which were supposed to obey the laws of classical Newtonian mechanics, and the physics of radiation, based on the idea of wave propagation in a hypothetical continuous medium, the luminous and electromagnetic ether. But these two systems of physics could not remain detached from each other: they had to be united by the formulation of a theory of exchanges of energy between matter and radiation. ... In the attempt to bring the two systems of physics together, conclusions were in fact reached which were neither correct nor even admissible. When applied to the energy equilibrium between matter and radiation ... Planck ... assumed ... that a light source ... emits its radiation in equal and finite quantities—in quanta. The success of Planck's ideas has been accompanied by serious consequences. If light is emitted in quanta, must it not, once emitted, possess a corpuscular structure? ... Jeans and Poincaré (showed) that if the motion of the material particles in a source of light took place according to the laws of classical mechanics, then the correct law of black-body radiation, Planck's law, could not be obtained.*

He also once talked about his discovery as follows:

> *As in my conversations with my brother we always arrived at the conclusion that in the case of X-rays one had both waves and corpuscles, thus suddenly— ... it was certain in the course of summer 1923—I got the idea that one had to extend this duality to material particles, especially to electrons. And I realised that, on the one hand, the Hamilton-Jacobi theory pointed somewhat in that direction, for it can be applied to particles and, in addition, it represents a geometrical optics; on the other hand, in quantum phenomena one obtains quantum numbers, which are*

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Box 1.8 (continued)

rarely found in mechanics but occur very frequently in wave phenomena and in all problems dealing with wave motion.

Thus I arrived at the following general idea which has guided my researches: for matter, just as much as for radiation, in particular light, we must introduce at one and the same time the corpuscle concept and the wave concept.

In other words, in both cases we must assume the existence of corpuscles accompanied by waves. But corpuscles and waves cannot be independent, since, according to Bohr, they are complementary to each other; consequently it must be possible to establish a certain parallelism between the motion of a corpuscle and the propagation of the wave which is associated with it.

De Broglie wrote many popular science books and was awarded first Kalinga Prize for the same in 1952 instituted by UNESCO.

This concept was initially hard to accept, as how can something be both wave and particle! However, later on, it turned out to be a very effective way of explaining various properties of atoms and subatomic particles like electrons, protons and neutrons. This concept of matter waves along with others discussed earlier laid down the foundation of quantum mechanics. 'Matter Waves' were not considered in classical mechanics.

1.3 Heisenberg's Uncertainty Principle

Additionally it is also necessary to consider 'uncertainty principle' put forth by W. Heisenberg in 1928. This also has no classical analogue but is one of the basic concepts in quantum mechanics.

In order to understand uncertainty principle, consider an experiment as follows. If we have a source of monochromatic light (single wavelength) at the back of two slits as shown in Fig. 1.6, we would obtain a diffraction pattern i.e. bands of dark and light areas. Dark bands correspond to the regions where light does not strike and light areas correspond to areas where light is able to reach. Replace now the source of light with source of mono energetic electrons from an electron gun. We would be able to see an interference pattern similar to that with light. We would get the diffraction pattern of light and dark regions by exposure of photographic plate to electrons. If we make few more experiments by reducing the electron beam intensity, we can see some interesting effect (Box 1.9).

Box 1.9: Interference of Light and Electrons

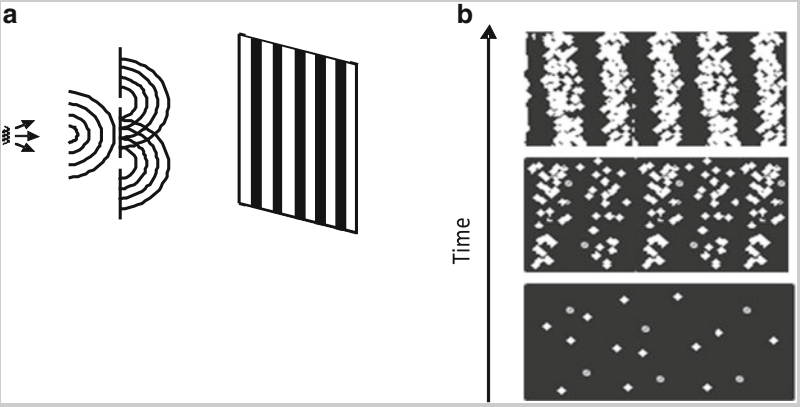


Fig. 1.6 (**a**) Schematic diagram to obtain diffraction pattern (slits S1 and S2) on the photographic plate P (one may use some counter also to detect the intensity). One can use photons or electrons as the source. (**b**) Electron diffraction pattern for change in exposure (counting) time

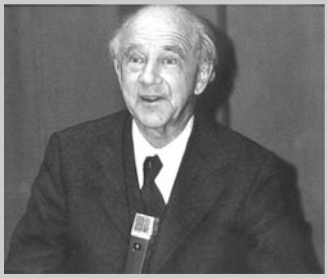
For much reduced intensity we would see blurred interference pattern and with further reduction of electron beam intensity we may get only a couple of spots and no bands of light and dark areas. However electrons appear to have gone to places where intensity maxima appear in diffraction pattern. The question is how do the electrons know to reach the places where intensity maxima occur? Through which slits the electrons go? If we reduce the intensity of beam such that within the exposure time of photographic plate only a single electron went through the slit, should it go to the region with maximum intensity when number of electrons were large and produced diffraction pattern similar to that of light? How should a single electron know what kind of pattern would be produced if more electrons were there and it should not go to certain regions? How does a single electron know about the presence of the other slit? Or did it exist at two slits simultaneously? This is perhaps hard to accept as we think of any particle or body having precise location at a precise time. This means that it would appear at one of the slits at a given time (classical mechanics concept).

Can we now think of an experiment to determine through which slit the electrons go to produce diffraction pattern? For this, we can perform an experiment in which we shine the slits with light. Suppose we illuminate the slits with X-rays of short wavelength for accurate measurement. By measuring the scattered radiation we should know through which slit the electrons passed. This would give us a result showing that 50 % electrons went through one slit and 50 % through the other. However we would see that there is no interference or diffraction pattern produced at all. Our new experiment has destroyed the interference pattern. This is because, as

we know, due to Compton effect electron changes its energy and direction. Without X-rays striking the electrons, they went to produce interference pattern or there were only certain momenta allowed for the electrons. After Compton scattering the electrons got other momenta from the photons so that they could reach the previously forbidden regions. On the other hand we can use very long wavelength. Location of electron can be determined with a precision of $\lambda/2$. If wavelength is very large, precision would be lost and we would not know through which slit the electron came out. In other words we cannot precisely know position and momentum of the electron simultaneously with arbitrary accuracy. If we reduce the momentum uncertainty (using long wavelength), position becomes uncertain and if we measure the position with certainty using short wavelength then momentum becomes uncertain destroying the diffraction pattern. Indeed it is not possible to keep both position and momentum measurement precise, simultaneously. Precise measurement of one disturbs the other measurement. This is known as Heisenberg's uncertainty principle (Box 1.10). It is expressed as

$$\Delta x.\Delta p \geq \frac{h}{2\pi} \tag{1.13}$$

Box 1.10: W. Heisenberg (1901–1976)
Werner Heisenberg was born on 5th December 1901 in Würzburg, Germany. His father became a Professor of Greek language in University of Munich and W. Heisenberg went to Munich. He completed his school studies in Munich but studied under eminent physicists like Sommerfeld, Wien, Rosenthal, Max Born, Hilbert etc. at various places.



In 1926 he was appointed as a lecturer under Niels Bohr and within a year as a Professor of theoretical physics at University of Leipzig in Germany. In 1929, he went to U.S., Japan and India to deliver a lecture series.

Heisenberg published theory of quantum mechanics at the age of just 23. He received the Nobel Prize in Physics for the theory he developed and specially its applications which resulted into the discovery of allotropes of hydrogen. Later he was interested in plasma physics. He also worked on the unified field theory of elementary particles. In 1941 he was appointed as a professor of physics at the University of Berlin and Director of Kaiser Wilhelm Institute of Physics. In later years he was in Munich and died in 1976.

where Δx is the dispersion $\left(= \sqrt{< (x - < x >)^2 >}\right)$ in the measurement of position in x direction and Δp is the dispersion in the simultaneous measurement of x component of momentum of a particle. It may be emphasized here that if we try to reduce the uncertainty in x or try to make a very precise measurement of position, the uncertainty in measurement of p increases and vice versa. The Eq. (1.13) is always valid irrespective of method of measurement. In other words, uncertainty principle gives the maximum possible accuracy in a simultaneous measurement of two quantities viz. position and momentum of a particle, in this case.

In general, Heisenberg's uncertainty principle states that "it is impossible to determine precisely and simultaneously the values of both the members of a particular pair of physical variables such as position components in a particular direction and momentum in that direction, energy of a bound state and its decay time etc."

1.4 Schrödinger Equation

In classical mechanics, in order to determine the position of a given particle under some conditions like its speed, initial velocity etc. we use Newton's equations. Similarly in quantum mechanics we make use of Schrödinger equation to understand the behaviour of subatomic particles (Box 1.11).

Box 1.11: Erwin Schrödinger (1887–1961)

Erwin Schrödinger was born on 12th August 1887, in Vienna, Austria. During his childhood he developed broad interests in various subjects from poetry to science. He studied from 1906 to 1910 in the University of Vienna. During World War I, he was an officer in artillery.

From 1920 he went on academic positions to various universities like in Stuttgart, Breslau and Zurich.

He worked on many problems in theoretical physics and produced significant work on atomic spectra, specific heats of solids, and physiological studies of colour. His greatest work, however, is the Schrödinger's wave equation which appeared in 1926 and he shared 1933 Nobel Prize for the same with Dirac. He however did not like the statistical interpretation of waves and generally accepted description in terms of waves and particles. In his own words:

(continued)

Box 1.11 (continued)

What we observe as material bodies and forces are nothing but shapes and variations in the structure of space. Particles are just schaumkommen (appearances). The world is given to me only once, not one existing and one perceived. Subject and object are only one. The barrier between them cannot be said to have broken down as a result of recent experience in the physical sciences, for this barrier does not exist. Let me say at the outset, that in this discourse, I am opposing not a few special statements of quantum mechanics held today (1950s). I am opposing as it were the whole of it. I am opposing its basic views that have been shaped 25 years ago, when Max Born put forward his probability interpretation, which was accepted by almost everybody. (Schrödinger Erwin, The Interpretation of Quantum Mechanics. Ox Bow Press, Woodbridge, CN, 1995).

I don't like it, and I'am sorry I ever had anything to do with it (Erwin Schrödinger talking about Born's Probability Wave Interpretation of Quantum Mechanics.)

In 1927 he went to Berlin but left it in 1933 when Hitler came into power. During World War II he moved to various places and settled in Dublin as director of School for Theoretical Physics. He returned to Vienna after he retired from there in 1955. He died on 4th January 1961.

For a free particle, in one dimension, time dependent Schrödinger equation is as follows:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} = i\hbar\frac{\partial\psi(x,t)}{\partial t} \tag{1.14}$$

where $\psi(x, t)$ is the wave function of particle of mass m. We neglect the potential energy V and assume that

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

which is the kinetic energy of the particle.

If we want to generalize the equation by writing $E =$ kinetic energy + potential energy

i.e.
$$E = \frac{\hbar^2 k^2}{2m} + V$$

the Schrödinger equation becomes

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x,t)\,\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t} \tag{1.15}$$

Equation (1.15) is one dimensional form of Schrödinger equation. A three dimensional form can be written as

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z,t)+V(x,y,z,t)\,\psi(x,y,z,t)$$
$$=i\hbar\frac{\partial\psi(x,y,z,t)}{\partial t} \tag{1.16}$$

We can use Laplacian notation viz.

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}=\nabla^2 \tag{1.17}$$

and **r** for (*x, y, z*).

Equation (1.16) takes then a compact form as

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t)+V(\mathbf{r},t)\,\psi(\mathbf{r},t)=i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} \tag{1.18}$$

This is a time-dependent Schrödinger equation in three dimensions.

We can also get a time independent Schrödinger equation as follows. In case the potential energy of a particle does not change with time (as in case of energy states of electrons in an atom), we can write for one dimension

$$V(x,t)=V(x) \tag{1.19}$$

and Schrödinger equation as

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x2}+V(x)\psi(x,t)=i\hbar\frac{\partial\psi(x,t)}{\partial t} \tag{1.20}$$

Assuming that wave function $\psi(x, t)$ can be separated into two parts viz. one varying with position and the other with time, it can be written as

$$\psi(x,t)=\mathbf{\Phi}(x)\boldsymbol{\theta}(t)$$

Substituting it in Eq. (1.20), we get

$$\frac{-\hbar^2}{2m}\boldsymbol{\theta}(t)\frac{d^2\mathbf{\Phi}(x)}{dx^2}+V(x)\mathbf{\Phi}(x)\boldsymbol{\theta}(t)=i\hbar\mathbf{\Phi}(x)\frac{d\boldsymbol{\theta}(t)}{dt} \tag{1.21}$$

or
$$\frac{-\hbar^2}{2m\mathbf{\Phi}(x)}\frac{d^2\mathbf{\Phi}(x)}{dx^2}+V(x)=\frac{i\hbar}{\boldsymbol{\theta}(t)}\frac{d\boldsymbol{\theta}(t)}{dt} \tag{1.22}$$

Note that in the above equation the left hand side is only position dependent and the right hand side is only time dependent. Therefore each side of the equation must be a constant, say *A*. We can therefore write

$$\frac{-\hbar^2}{2m\mathbf{\Phi}(x)}\frac{d^2\mathbf{\Phi}(x)}{dx^2}+V(x)=A \tag{1.23}$$

and $$\frac{i\hbar}{\boldsymbol{\theta}(t)}\frac{d\boldsymbol{\theta}(t)}{dt} = A \tag{1.24}$$

Solving Eq. (1.24), we obtain

$$\boldsymbol{\theta}(t) = \boldsymbol{\theta}(0)e^{\frac{-iAt}{\hbar}} \tag{1.25}$$

where $\theta(0)$ is $\theta(t)$ at time $t = 0$.

Value of constant A can be found out as follows.

Compare equation

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

and

$$\frac{i\hbar}{\boldsymbol{\theta}(t)}\frac{d\boldsymbol{\theta}(t)}{dt} = A$$

They are similar at $x = 0$. This implies that $A = E$. Therefore Eq. (1.24) can be rewritten as

$$\frac{d\boldsymbol{\theta}(t)}{\boldsymbol{\theta}(t)} = -iE\frac{dt}{\hbar} \tag{1.26}$$

Integrating it, we obtain

$$\boldsymbol{\theta}(t) = \exp\left(\frac{-iEt}{\hbar}\right) \tag{1.27}$$

Substituting A in Eq. (1.23) with E now, we get

$$\frac{-\hbar^2}{2m\boldsymbol{\Phi}(x)}\frac{d^2\boldsymbol{\Phi}(x)}{dx^2} + V(x) = E \tag{1.28}$$

or $$\frac{-\hbar^2}{2m}\frac{d^2\boldsymbol{\Phi}(x)}{dx^2} + V(x)\boldsymbol{\Phi}(x) = E\boldsymbol{\Phi}(x) \tag{1.29}$$

This is one dimensional, time independent Schrödinger equation. For three dimensions we can write

$$\psi(\mathbf{r},t) = \psi(\mathbf{r})\,\boldsymbol{\Phi}(t) \tag{1.30}$$

and time independent three dimensional Schrödinger equation becomes

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\,\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{1.31}$$

In order to determine the energy states of a particle it is necessary to know the form of potential V and how particle amplitude varies in space or $\psi(\mathbf{r})$. There may be a number of wave functions satisfying Schrödinger equation, but all may not be able to describe a given situation. The acceptable wave function should satisfy physical boundary conditions. It is necessary that ψ should satisfy following conditions so that using Schrödinger equation one can obtain the realistic values of energy.

1. $\psi(\mathbf{x}, \mathbf{y}, \mathbf{z})$ must be finite and single valued at all points in coordinate space.
2. It is necessary that $\psi(x, y, z)$ is a continuous function at all points in coordinate space.
3. Derivatives of ψ viz. $\frac{\partial\psi}{\partial x}$, $\frac{\partial\psi}{\partial y}$ and $\frac{\partial\psi}{\partial z}$ also need to be finite, single valued and continuous functions in coordinate space.
4. $\int |\psi|^2 d\tau$ must be finite, where $d\tau$ is the volume.

It is convenient to use complex wave form of ψ.

$$\psi = u + iv \text{ with } u \text{ and } v \text{ as real functions.} \tag{1.32}$$

$$\psi^* = u - iv \text{ is the complex conjugate of } \psi. \tag{1.33}$$

$$\psi\psi^* = u^2 + v^2 \tag{1.34}$$

Although ψ and ψ^* do not have physical significance as such, $\psi\psi^*$ or $|\psi|^2$ is interpreted as the probability density of particle being there in integration limits of $\int |\psi|^2 d\tau$ (Box 1.12).

Box 1.12: Physical Interpretation of de Broglie Wave

1. The wave function $\psi(\mathbf{r}, t)$ is useful to determine the probability of finding a moving particle.
2. $\psi(\mathbf{r}, t)$ may be complex.
3. $|\psi(\mathbf{r}, t)|^2$ is the probability of finding the particle at time t at a point given by $\mathbf{r}$ in real space.
4. As the particle should be found somewhere in space it can be obtained using the normalization condition $\int |\psi(\mathbf{r}, t)|^2 d\tau = 1$.

1.5 Electron Confinement

As briefly mentioned in the introduction of this chapter, nano structured materials have at least one of the dimensions in the range of 1–100 nm. In such cases properties of materials can be understood using quantum mechanics rather than classical mechanics. Even the properties of atoms, molecules or extended solids can be understood using quantum mechanics because in order to understand various

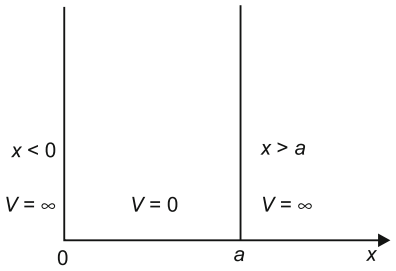


Fig. 1.7 One dimensional potential box

properties even in case of bulk solids we need to understand the electron properties which are subatomic particles. For detailed descriptions it is necessary to refer to books devoted to atoms and molecules and solid state physics. Here we shall outline the essential features by which one can understand the methodology.

We shall discuss in this section confinement of a particle in one dimension (freedom in 2D), confinement in two dimensions (freedom in 1D) and confinement in all three dimensions (no freedom in any direction or 0D material). These confinements when referred to practical cases are often known as essentially 2D quantum wells (thin film), 1D wire (wire) and 0D quantum dot (nanoparticles).

1.5.1 Particle in a Box

Consider a box of length 'a' such that

Potential	$V = 0$	if $0 < x < a$
and	$V = \infty$	if $x < 0$ or $x > a$

as illustrated in Fig. 1.7.

Energy states of the particle of mass m can be obtained using time independent Schrödinger equation for one dimension as

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E\psi(x) \tag{1.35}$$

Let $\psi(x)$ have a general form as

$$\psi(x) = A\sin\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}x + B\cos\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}x \tag{1.36}$$

As the particle exists only inside the box, wavefunction should not exist outside the box and should be zero at the boundaries.

At $x = 0$, boundary condition $\psi(x) = 0$ leads to $B = 0$. Therefore,

$$\psi(x) = A\sin\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}x \tag{1.37}$$

At $x = a$, boundary condition $\psi(a) = 0$ leads to

$$\psi(a) = 0 = A \sin \left(\frac{2mE}{\hbar^2} \right)^{\frac{1}{2}} a \tag{1.38}$$

But 'a' is not zero, therefore

$$\sin \left(\frac{2mE}{\hbar^2} \right)^{\frac{1}{2}} a = 0 \quad \text{or,} \quad \left(\frac{2mE}{\hbar^2} \right)^{\frac{1}{2}} a = n\pi$$

where $n = 0, 1, 2, 3, \ldots$

Therefore

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2ma^2} = \frac{n^2 h^2}{8ma^2} \tag{1.39}$$

i.e., $$E_n \propto n^2 \tag{1.40}$$

Putting E_n in Eq. (1.37) we get

$$\psi_n = A \sin \left(\frac{n\pi}{a} \right) x \tag{1.41}$$

Although n can take any integer value according to Eq. (1.39), in practice $n = 0$ and $\psi_n = 0$ are not allowed inside the box, because, if allowed, $|\psi|^2$ would be 0 and probability of finding the particle inside the box would be zero. For the same reason ψ cannot be zero inside the box. Therefore n takes the values $n = 1, 2, 3, \ldots$. This shows that energies of particle in a one dimensional potential box are quantized and can be illustrated as in Fig. 1.8a.

Corresponding wave functions and probabilities of different states of particle in the box would look like those in Fig. 1.8b, c respectively.

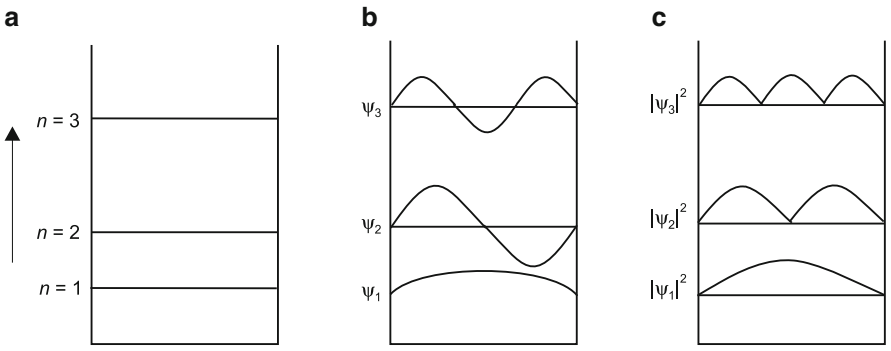


Fig. 1.8 (**a**) Quantized energy states, (**b**) corresponding wavefunctions and (**c**) probability of finding the particle at different locations between '0' and 'a' in the box

1.5.2 Density of States

Density of states *D(E)* is an important quantity. It enables to gain understanding of various spectroscopic and transport properties of materials. It is defined as the number of states per unit energy range and in general can be obtained as follows. Consider energy as is given for a particle in a 1D box.

$$E_n = n^2 = \frac{h^2}{8ma^2} \quad \text{(Henceforth we drop suffix of } E\text{)}$$

$$dE = \frac{h^2}{8ma^2}.2n.dn \tag{1.42}$$

$$\frac{dn}{dE} = \frac{8ma^2}{h^2}.\frac{1}{2n} = \frac{a}{h}\sqrt{\frac{2m}{E}} \tag{1.43}$$

$$D(E) = \frac{dn}{dE} \propto E^{-1/2} \tag{1.44}$$

The Eq. (1.44) shows how the density of states will vary with change of energy. Depending upon the energy state's function, density of states would take form as briefly stated below.

1.5.2.1 Density of States for a Zero Dimensional (0D) Solid

Neglecting the periodic potential existing in solids, we can imagine a zero dimensional solid in which electron is confined in a three dimensional potential box with extremely small (<100 nm) length, breadth and height as a 0D solid. This will have the discrete energy levels as discussed above with density of states given as

$$D(E) = \frac{dN}{dE} = \sum_{\varepsilon_i} \delta\left(E - \varepsilon_i\right) \tag{1.45}$$

where ε_i are discrete energy levels and δ is Dirac function. The density of states as a function of energy would appear as illustrated in Fig. 1.9.

1.5.2.2 Density of States in a One Dimensional (1D) Potential Box, Wire

A particle confined in one dimension is like a particle in a one dimensional potential well as in the previous case. However the potential in two directions is infinitely large but length is not very small. This gives rise to density of states as follows:

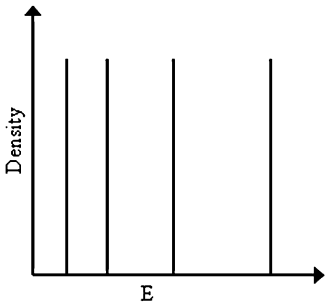


Fig. 1.9 Density of states for a particle in a zero dimensional solid

$$D(E) = \frac{dN}{dE} = \sum_{\varepsilon_i < E} \delta(E - \varepsilon_i)^{-1/2} \tag{1.46}$$

where ε_i are discrete energy levels. Figure 1.10 graphically illustrates nature of density of states for a one dimensional solid.

1.5.2.3 Density of States in a Two Dimensional (2D) Potential Box, Thin Film

It can be shown that the density of states ($D(E)$) in the two dimensional solid, which is nothing but the case of thin films, is given as

$$D(E) = \frac{dN}{dE} = \sum_{\varepsilon_i < E} 1 \tag{1.47}$$

Thus it can be shown that the density of states in two dimensional case is constant (see Fig. 1.11). In this case $\frac{dN}{dE}$ would correspond to the states available in an area.

1.5.2.4 Density of States for a Particle in a Three Dimensional Box

Following the previous cases it is a straightforward task to show that in a box of length 'a', width 'b', and height 'c' with potential $V = 0$ inside the box and $V = \propto$ outside the box, the energy states can be obtained as

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{2m}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{1.48}$$

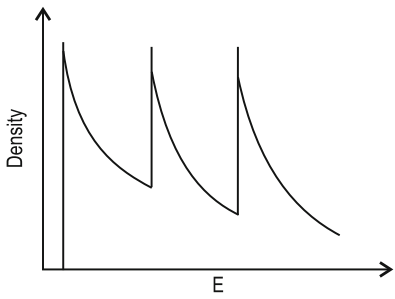


Fig. 1.10 Density of states for a particle in a one dimensional solid

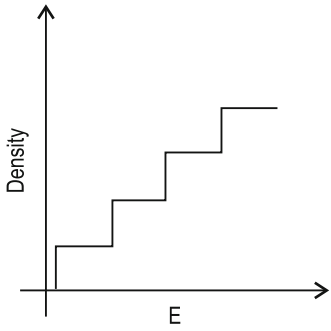


Fig. 1.11 Density of states for a 2D potential box

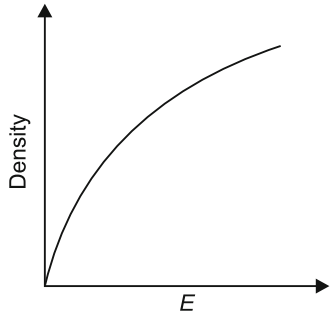


Fig. 1.12 Density of states for a particle in a 3D potential box

The wave function has the form

$$\psi_n(x, y, z) = A \sin\left(\frac{\pi n_x x}{a}\right) \sin\left(\frac{\pi n_y y}{b}\right) \sin\left(\frac{\pi n_z z}{c}\right) \tag{1.49}$$

Hence to consider the density of states we shall require the volume. It can be shown that

$$D(E) \propto E^{1/2} \tag{1.50}$$

This is graphically illustrated in Fig. 1.12.

1.5.3 Particle in a Coulomb Potential

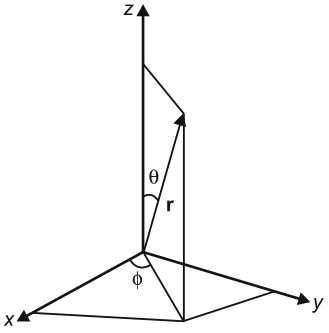
So far we have considered the particle confined to a potential box in which $V = 0$ inside the box and abruptly outside the box $V = \propto$. We shall consider now another type of potential viz. Coulomb potential experienced by a particle. The potential can be written as

$$V(r) = \frac{-Ze^2}{r} \tag{1.51}$$

This type of potential can arise when a particle moving in three dimensions is attracted towards the centre. For example an electron with negative charge attracted towards a positively charged nucleus at the centre of an atom.

In Eq. (1.51) 'Ze' is the charge due to Z number of electrons and r is the distance between nucleus and the charge. The negative sign arises by convention to show attraction between oppositely charged particles.

It is convenient to solve this problem in spherical coordinates rather than in Cartesian coordinates by writing ψ, the wave function in spherical coordinates $\psi(r, \theta, \varphi)$.



$$x = r \sin\theta \cos \phi \tag{1.52}$$

$$y = r \sin\phi \sin \theta \tag{1.53}$$

$$z = r \cos \theta \text{ and } r = \sqrt{x^2 + y^2 + z^2} \tag{1.54}$$

The time independent Schrödinger equation in spherical coordinates can be written as

$$\nabla^2 \psi(\mathbf{r}, \theta, \phi) + \frac{2m}{\hbar^2}[E - V(\mathbf{r})]\psi(\mathbf{r}, \theta, \phi) = 0 \tag{1.55}$$

We shall not go here in the details of solving this equation but state the major steps and result. It is the spherically symmetric form of the potential which enables us to simplify the procedure.

Wavefunction $\psi(\mathbf{r},\theta,\phi)$ is separable into functions of $\mathbf{r}$, θ and φ as

$$\psi = R(r)Y(\theta, \varphi) \tag{1.56}$$

It can be written as

$$\psi_{n\ell m}(r, \theta, \phi) = \frac{U_{n\ell}(r)}{r} Y_{\ell m}(\theta, \varphi) \tag{1.57}$$

$Y_{\ell m}$ are spherical functions.

The energy states can be obtained by considering one dimensional form of Eq. (1.55) as follows

$$\frac{-\hbar^2}{2m}\frac{d^2U}{dr^2} + \left[V(r) + \frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]U = EU \tag{1.58}$$

Energy state of the system is described with three quantum numbers: n (principal quantum number), ℓ (orbital quantum number) and m (magnetic quantum number).

The angular momentum of the state is given by L, as

$$L^2 = \ell(\ell+1)\hbar^2 \text{ where } \ell = 0, 1, 2, \ldots (n-1) \tag{1.59}$$

The magnetic quantum number m essentially gives component of angular momentum L parallel to z axis as

$$L_z = m\hbar \text{ where } m = 0, \pm 1, \pm 2, \cdots \pm \ell \tag{1.60}$$

The states are often denoted by $s, p, d, f \ldots$ to mean $\ell = 0, 1, 2$ etc. respectively.

If we consider now a Coulomb potential experienced by an electron of the form

$$V(r) = \frac{-Ze^2}{r}$$

where Z is atomic number, a situation in hydrogen atom (H), helium ion (He^+), lithium ion (Li^{2+}) etc.

Corresponding Schrödinger equation can be written as

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0 \tag{1.61}$$

The energy states by solving the equation in spherical coordinates gives

$$E_n = \frac{-2\pi^2 \mu Z^2 e^4}{n^2 h^2} \tag{1.62}$$

where m is the electron mass corrected for motion of nucleus

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M} \tag{1.63}$$

Note that n is an integer which takes the values,

$$\begin{aligned} n &= \ell + 1, \ell + 2, \ell + 3 \ldots \\ \ell &= 0, 1, 2, 3 \ldots (n-1) \end{aligned} \tag{1.64}$$

One can see here that E_n is proportional to $1/n^2$, which means that energies will come closer as n increases, as opposed to potential in a box with potential inside as zero.

1.6 Tunnelling of a Particle Through Potential Barrier

Consider a situation in which a matter wave is incident on a potential barrier as illustrated in Fig. 1.13 from negative x direction. For the sake of simplicity, we shall consider one dimensional case. Energy of the particle is purely kinetic in region I and potential $V = 0$. However, $E < V_0$ in region I, where V_0 is the potential at $x = 0$. It can be shown using Schrödinger equation that for particle with less energy than the potential energy as in region I, there certainly exists a possibility that particle can not only enter the region II but also get transmitted in region III and propagate as long as V_0 is not infinite. This is impossible in classical mechanics. To understand

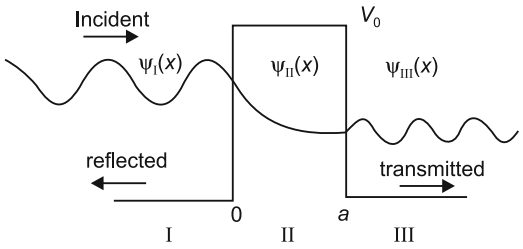


Fig. 1.13 Particle tunnelling through a potential barrier of height V_0. The kinetic energy of the particle is $E < V_0$. The particle is incident from left side in region I and by tunnelling through region II, escapes to region III with some probability of transmission, given by Eq. (1.73)

this phenomenon of 'tunnelling' in quantum mechanics, consider that we have three different wave functions in regions I, II and III as follows

$$\psi_{\mathrm{I}}(x) = A_1 e^{ikx} + A_2 e^{-ikx} \tag{1.65}$$

$$\psi_{\mathrm{II}}(x) = B_1 e^{\alpha x} + B_2 e^{-\alpha x} \tag{1.66}$$

$$\psi_{\mathrm{III}}(x) = C_1 e^{ikx} + C_2 e^{-ikx} \tag{1.67}$$

In all these wave functions we have considered that wave function is composed of two parts viz. a wave in positive direction (denoted by e^{ikx} and $e^{\alpha x}$) and negative direction (denoted by e^{-ikx} and $e^{-\alpha x}$). Waves in regions I and III are travelling waves (but that in region II is only decaying part) as

$$k = \sqrt{\frac{2mE}{\hbar^2}} \tag{1.68}$$

and

$$\alpha = \sqrt{\frac{2m\,(V_0 - E)}{\hbar^2}} \text{are positive.} \tag{1.69}$$

We now need to use boundary and normalization conditions to determine the coefficients A_1, A_2, B_1, B_2, C_1 and C_2 in Eqs. (1.65), (1.66), and (1.67). We may further note that in region I, there is a probability that incident wave gets reflected but in region III there is no reflection. It can be shown after solving the equations that we can get tunnelling probability T defined as

$$T = \frac{|\psi_{III}(x)|^2}{|\psi_I \text{ (incident)}|^2} = \frac{{C_1}^2}{A_1^2} = \frac{1}{1 + D\sinh^3(\alpha a)} \tag{1.70}$$

with

$$D = \frac{V_0^2}{4E\,(V_0 - E)}. \tag{1.71}$$

If $\alpha a \gg 1$ i.e. potential barrier V_0 is extremely higher and the barriers width is very large, then we can use an approximation

$$\sinh\,\alpha a \approx \frac{1}{2} e^{\alpha a} \tag{1.72}$$

In this case it can be shown that

$$T = T_0 e^{-2\alpha a} \tag{1.73}$$

where

$$T_0 = \frac{16E\,(V_0 - E)}{V_0^2}. \tag{1.74}$$

Thus we can notice that there is always a probability of finding the particle on the other side of a potential barrier even though its kinetic energy is less than the potential barrier it sees. This result is very useful in understanding many phenomena observed for subatomic particles and cannot be explained by classical mechanics.

One can also show that reflection probability of wave in region I is

$$R = \frac{{A_2}^2}{{A_1}^2} = 1\text{–}T \tag{1.75}$$

As mentioned earlier, the phenomenon of tunnelling through a potential barrier is possible only in quantum mechanics with no classical analogue. This means that a particle with kinetic energy smaller than that required to overcome the potential energy of the barrier does have some probability of being on the other side of the barrier. This is quite important to explain quantum well structures, solid state lasers, light emitting diodes, particles inside the nucleus etc.

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