LECTURE 9 THERMAL RADIATION AND ORIGINS OF QUANTUM THEORY

Topics
- Origins of Quantum theory- A historical perspective
- Black body radiation
- Failure of classical mechanics with respect to black body radiation
- Planck’s law and the black body radiation
- Photoelectric effect
- Heat Capacity
- The hydrogen atom- Atomic Spectra and the Neil Bohr’s atomic model
- Correspondence principle
- De Broglie’s hypothesis: - Particle-wave duality
- Wave Mechanics

OBJECTIVES
At the end of this lecture you should be able to;

1) Distinguish between classical physics and quantum physics
2) Point out experimental observations (features) about blackbody radiation, photoelectric effect, heat capacity and hydrogen atomic spectrum that could not be explained by classical physics.
3) Use quantum theory to explain features mentioned in (2) above
4) State the Wilson-Sommerfeld quantization notes and apply the same to derive the Planck’s quantization law and the Bohr’s quantization rule.
5) State the correspondence principle and explain its significance.
6) State the concept of wave-particle duality, and explain why wave-nature of matter is not observed in daily life.
7) State and apply the uncertainty principle
8) Provide the probabilistic interpretation of de Broglie waves.
9.1 Origins of the Quantum Theory

Beginnings of quantum theory is placed at about 1900, the year Max Planck gave a formula for the distribution of energy in terms of frequency in blackbody radiation. His formula introduced a new concept, i.e., the Planck’s constant \( h \) or \( \left( \frac{h}{2\pi} \right) \).

At this stage we need to remind ourselves of the following:

1. Newtonian mechanics: In classical physics matter is comprised of point particles that move under the action of interacting forces that obey Newton’s laws. The most important law being the law of motion: \( F = ma \), \( F \) being the force, \( a \) the acceleration and \( m \) the mass.

The motion of electrically neutral macroscopic systems have been explained satisfactorily by classical physics using the Newton’s law of motion, together with the law of gravity. In these macroscopic systems, matter is treated in terms of definite mass, and the motion of the particle is defined in terms of its energy, \( E \) and momentum, \( \mathbf{P} \).

2. Electromagnetic theory: As a component of the classical theory, it is concerned with electric and magnetic phenomena, and these are described in terms of electric and magnetic fields \( \mathbf{E}(x) \) and \( \mathbf{B}(x) \) respectively, which, are related by the Maxwell’s equations.

Prior to the development of the quantum theory, electromagnetic energy, which we now know to be quantized, i.e., comes in discrete lumps, or packets or quanta (photons) were regarded as continuous. This quantization manifests itself in the processes of absorption or emission by matter of radiation, which occurs only in multiple units of these packets.

9.2 Breakdown of classical concepts

In this section we shall consider some experimental results that could not be explained by classical physics and proceed to discuss how they were eventually explained.

9.2.1 Blackbody Radiation

A black body is defined as one that absorbs all incident electromagnetic radiation. The frequency distribution of the radiation spectrum from a blackbody depends only on the temperature and not the material of that body.

Attempts to explain the blackbody radiation using classical theory failed. According to the classical theory, the exchange of energy between radiation and matter was assumed to be continuous, in the sense that light of a frequency \( v \) can
give up any amount of energy on absorption, the amount in any particular case being dependent on the intensity of the beam.

Fig. 9.1. Radiation density for a blackbody radiation

The following information is important know

a) Stefan’s law: The rate of energy loss from a hot body is proportional to $T^4$, where $T$ is the absolute temperature.

$$E = \frac{4\delta}{c} T^4$$  \hspace{1cm} (9.1)

where $\delta = 5.6 \times 10^{-8} \text{W/m} \cdot \text{K}^4$ is the Stefan’s-Boltzmann constant, $c$ is the velocity of light, and $E$ is the total radiation density.

b) Wien’s displacement law: The wavelength, which is emitted with maximum intensity from a blackbody is proportional to $T^4$, that is,

$$\lambda_{\text{max}} \propto \frac{1}{T} \text{ or } \lambda_{\text{max}} T = \text{constant}$$  \hspace{1cm} (9.2)

In other words, the spectrum shifts to higher frequencies (lower wavelengths) as temperature increases (see Fig. 9.1).
Based on classical electromagnetic theory, Rayleigh and Jeans derived an equation known as the Rayleigh-Jeans formula:

\[ E(v)dv = \frac{8\pi v^2}{c^3} kTd\nu \quad \text{or} \quad E(\lambda) d\lambda = \frac{8\pi}{\lambda^4} kTd\lambda \quad (9.3) \]

where \( E(\lambda)d\lambda \) is the energy density of radiation per unit volume with wavelengths between \( \lambda \) and \( \lambda + d\lambda \), \( k \) is the Boltzmann’s constant and \( T \) is the absolute temperature.

The Rayleigh-Jean’s law implies that the energy radiated in a given wavelength range \( d\lambda \) increases limitlessly as the wavelength becomes smaller (see Fig. 9.1). This is in contradiction to the experimental results, except in the long-wavelength region.

From Eqn (9.3)

\[ E(v) = \int_0^\infty E(v)dv = \frac{8\pi}{c^3} kT \int_0^\infty v^2dv \quad (9.4) \]

which implies that \( E \) is finite. It is thus observed that the Rayleigh-Jean’s law requires that the total energy radiated per unit volume is infinite at all temperatures except at \( T = 0 \). This is incorrect, and is often referred to as the ultra-violet catastrophe. This is a pointer to a fundamental error in the classical theory.

It was Max Planck who provided a correct radiation formula by assuming that the energy exchange is discrete. That is, the radiation of frequency \( v \) can only exchange energy with matter in units of \( hv \), where \( h \) is a universal constant.

**Planck’s constant** \( h = 2\pi\hbar = 6.62 \times 10^{-34} \text{ joule – sec} \).

Planck’s hypothesis is thus stated as: The radiation of frequency \( v \) behaves like a stream of particles (photons) of energy.

\[ E = hv = h\omega \quad (9.5) \]

where \( \omega = 2\pi v \). Thus in an oscillator of frequency \( v \), the only permitted values of energy are

\[ E = nhv, \quad n = 1,2,3, \ldots \quad (9.6) \]

Equation (9.5) is a fundamental formula of quantum mechanics, and it can be seen from it that the high-frequency (short-wavelength) photons are the most energetic. For light
\((\nu = 10^5 \text{Hz}), E = 10^{-18} J\). This is negligible in the macroscopic world. Hence Eqn. (9.5) is only of importance at the atomic (microscopic) scale.

It can be shown that the **average energy** of a quantized oscillator is

\[
\overline{E} = \frac{hv}{e^{hv/kT} - 1} .
\]  

(9.7)

**Example:**

Calculate average energy of an oscillator if its frequency is \(5.0 \times 10^{14} \text{Hz}\) and temperature is 5000 K.

**Solution**

From the given parameters, we have

\[ h\nu = 6.63 \times 10^{-34} \text{J.s} \times 5.0 \times 10^{14} \text{s}^{-1} = 3.32 \times 10^{-19} J \]  
and

\[ kT = 1.38 \times 10^{-23} J / K \times 5000K = 6.90 \times 10^{-20} J \]

Hence

\[
\overline{E} = \frac{hv}{e^{hv/kT} - 1} = \frac{3.32 \times 10^{-19} J}{\exp(3.32 \times 10^{-19} J / 6.90 \times 10^{-20}) - 1} = 2.7 \times 10^{-21} J
\]

Notice that this energy is much smaller than \(kT\).

Another important relation between \(E\) and momentum \(\vec{P}\) is given by

\[
\vec{P} = \hbar \vec{k}
\]  

(9.8)

where \(\vec{k} = \frac{2\pi}{\lambda}\) is the wave number (vector).

Equations (9.5) and (9.8) show the relation between the particle parameters \((E, \vec{P})\) of the photon, and the parameters \((\omega, \vec{k})\) of the corresponding wave.

The Planck’s relation for the density of radiation (shown in Fig. 9.1) is

\[
E(\nu) d\nu = \frac{4\pi \nu^2}{c^3} \left( \frac{hv}{e^{hv/kT} - 1} \right) d\nu
\]  

(9.9)

or
These equations agree quite well with the observed radiation distribution when \( h \) is chosen correctly. In the long wavelength limit (low frequencies)

\[
e^{\frac{hv}{kT}} \approx 1 + \frac{hv}{kT}
\]

and Planck’s relation reduces to the Rayleigh-Jeans Law.

The total radiation density arising from all frequencies is obtained from Eqns. (9.9) or (9.10) thus

\[
E = \int_{0}^{\infty} E(v)dv = \frac{8 \pi^5 k^4}{15 \cdot 15 c^3 \hbar^3} T^4
\]

Equation (9.11) shows that the energy density is proportional to \( T^4 \), as first suggested by Stefan (Eqn. 9.1).

### 9.2.2 Photoelectric Effect

This is the ejection of electrons from the surface of a metal when a beam of monochromatic light of some frequency \( (v) \) is shone on the surface. This phenomenon provided a direct confirmation of energy quantization of em fields. If \( h\omega < \Phi \), (the work function, defined as the work required to free the electron from the attractive potential produced by the metal, depends on a particular metal) no electrons are emitted over a wide range of intensities of the beam. If \( h\omega > \Phi \), electrons are emitted with kinetic energy \( T \), such that

\[
h\omega = \Phi + T
\]

\( T \) does not depend on the intensity of radiation but only on its frequency. This observation cannot be explained by the classical theory, which assumes a continuous exchange of energy. The phenomenon of photoelectric effect was explained by Einstein who invoked the concept of the em field particles (photons) carrying energy \( hv (or h\omega) \), that is, the energy is transmitted by photons.
Features of the photoelectric effect that cannot be explained by the classical theory are:

1) Wave theory predicts that the oscillating electric field vector \( \vec{E} \) of the light wave increase in amplitude as intensity of the light beam increases. That is, since the force on the electron equals \( e\vec{E} \), then the kinetic energy of the photoelectrons should increase as intensity increases. It is however, observed that \( T_{\text{max}} \) is independent of intensity.

2) Wave theory predicts that the photoelectric effect should occur for every frequency of light as long as the intensity is adequate to provide enough energy to eject the electrons. This is not observed. There is a characteristic cut off frequency \( (v_o) \) below which no electrons are emitted.

3) There is no time lag between the moment then light starts to impinge on the target and when the photoelectron is ejected, that is, electrons are ejected almost instantaneously even in dim light.

Note that from equation (9.12)

\[
T_{\text{max}} = hv - \Phi
\]

or

\[
eV = hv - \Phi \Rightarrow V = \frac{hv - \Phi}{e}
\]  

(9.13)
Thus Einstein theory predicts a linear relationship between the stopping potential \( (V) \) and the frequency \( (\nu) \) as found experimentally.

**The photoelectric effect and blackbody radiation show only that energy exchange takes place by quanta \( h\nu \).**

**Example.** The work function for zinc is 4.24 eV. Determine the cut-off frequency for the ejection of photoelectrons from zinc.

**Solution.** At the cut-off frequency the kinetic energy is zero. Thus from Eqn (9.13) we get

\[
0 = h\nu - \Phi
\]

or

\[
\nu = \frac{h}{\Phi} = \frac{4.24 \times 1.60 \times 10^{-19} \text{J}}{6.63 \times 10^{-34} \text{J.s}} = 1.02 \times 10^{15} \text{Hz}
\]

**Activity:**

List the key features of the photoelectric effect

### 9.2.3 Heat Capacity of Solids

This again is one of the experimental results that could not be explained by classical physics.

![Graph](image)

**Figure 9.3** Variation of heat capacity with temperature
Classically an average total energy of $3kT$ is attached to each atom and of $3NkT$ for each mole of solid. Thus

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v = \frac{\partial (3NkT)}{\partial T} = 3Nk$$  \hspace{1cm} (9.14)

Equation (9.14) expresses the Dulong-Petit law. The explanation for the fall of $C_v$ at low temperatures was first given by Einstein, and later in more details by Debye. The fundamental assumption of Einstein or Debye theories is that the solid can be viewed as a set of oscillators vibrating with a characteristic frequency according to the relation

$$E = \left( n + \frac{1}{2} \right)\hbar
$$  \hspace{1cm} (9.15)

when $n$ is an integer.

Einstein assigned each oscillator an average energy per direction, $\overline{E} = \frac{\hbar \nu}{e^{\hbar \nu / kT} - 1}$. (Recall equation 9.7). Multiplying this equation by the Avogadro’s number and by a factor 3 to account for the three directions, the energy per mole is obtained, i.e.,

$$\overline{E}_{\text{mole}} = \frac{3N\hbar \nu}{e^{\hbar \nu / kT} - 1}$$  \hspace{1cm} (9.16)

When we differentiate equation (9.16) w.r.t temperature we get

$$C_v = \frac{d \overline{E}_{\text{mole}}}{dT} = 3R \left( \frac{\hbar \nu}{kT} \right)^2 \frac{e^{\hbar \nu / kT}}{(e^{\hbar \nu / kT} - 1)^2}$$  \hspace{1cm} (9.17)

which matched the experimental results pretty well.

**Activity**

1. Using the Dulong-Petit law, calculate the value of $C_v$ per mole.
2. Differentiate equation (9.16) with respect to temperature to arrive at equation (9.17). Show all steps fully.
9.3 The Hydrogen Atom- The Atomic Spectra

Having discussed some of the experimental results that could not be explained by classical physics, and seen how they were only explained by introducing radically new ideas, we revert back to some experimental results alluded to in Lecture one, especially when we discussed the Bohr’s model of an atom. That is, we look into more details the atomic spectra and point out certain experimental observations and theories put forward to explain them. We shall notice that the more successful formulations are those that introduce the concept of quantization.

When an electric discharge is passed through a monatomic gas, then because of the collisions with electrons, and with each other, some of the atoms in the discharge are excited into a state in which the total energy exceeds that in a normal atom. Upon returning to their normal state, these excited atoms give up their excess energy in the form of electromagnetic radiation. If this radiation is collimated and passed through a prism (or diffraction grating) it is broken up into its wavelength spectrum, which can be recorded on a photographic plate.

*It is observed that contrary to the expected continuous spectrum of electromagnetic radiation emitted, the spectrum of the em radiation emitted by free atoms is concentrated at a certain number of discrete wavelengths.* Each of these wavelength components is called a line because of the line it produces on the photographic plate.

![Figure 9.4 Visible spectrum of the hydrogen atom](image)

It has been observed that each kind of atoms has its own characteristics spectrum i.e., unique set of wavelengths at which the lines of the spectrum. Balmer’s equation is

Balmer discovered a striking relationship between the frequencies of the most prominent lines of the hydrogen spectrum. Balmer’s equation is
\[ \lambda = 3646 \frac{n^2}{n^2 - 4} \text{ (in units of Å)} \] 

(9.18)

where \( n (=3,4,5 \text{ etc}) \) is an integer.

In a slightly rewritten form due Rydberg the frequencies \( \nu \) are given by the formula

\[ \frac{1}{\lambda} = R_H \left( \frac{1}{\frac{2^2}{n^2}} - \frac{1}{n^2} \right) \] 

(9.19)

where \( n \) takes the integral values \( 3,4,5 \text{ etc} \) and \( R_H (= 10967757.6 \text{m}^{-1}) \) is the Rydberg constant. Formulae of the form of Eqn.(9.19) are known to exist. For example

<table>
<thead>
<tr>
<th>Name</th>
<th>Wavelength Range</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyman</td>
<td>Ultraviolet (UV)</td>
<td>( \lambda^{-1} = R_H \left( \frac{1}{\frac{1^2}{n^2}} - \frac{1}{n^2} \right), n=2,3 \ldots )</td>
</tr>
<tr>
<td>Balmer</td>
<td>Near UV and visible</td>
<td>( \lambda^{-1} = R_H \left( \frac{1}{\frac{2^2}{n^2}} - \frac{1}{n^2} \right), n=3,4 \ldots )</td>
</tr>
<tr>
<td>Paschen</td>
<td>Infrared</td>
<td>( \lambda^{-1} = R_H \left( \frac{1}{\frac{3^2}{n^2}} - \frac{1}{n^2} \right), n=4,5 \ldots )</td>
</tr>
<tr>
<td>Brackett</td>
<td>Infrared</td>
<td>( \lambda^{-1} = R_H \left( \frac{1}{\frac{4^2}{n^2}} - \frac{1}{n^2} \right), n=5,6 \ldots )</td>
</tr>
<tr>
<td>Pfund</td>
<td>Infrared</td>
<td>( \lambda^{-1} = R_H \left( \frac{1}{\frac{5^2}{n^2}} - \frac{1}{n^2} \right), n=6,7 \ldots )</td>
</tr>
</tbody>
</table>

As the wavelength decreases, the lines are found closer together and weaker in intensity until the series limit at 3646 Å is reached beyond which there are no separate lines but only faint continuous spectrum.

### 9.3.1 Bohr’s atomic model and the atomic spectrum

Recall the Bohr’s proposals that

1. An electron in an atom can revolve about the nucleus only in certain allowed orbits which may be circular or elliptical. Each allowed orbit represents a stationary energy. Thus the total energy \( E \) remains constant. This postulate is in contrast to the prediction of classical theory.

The allowed orbits or states are those in which angular momentum \( (L) \) of the electron about the nucleus is an integral multiple of \( \hbar = \frac{h}{2\pi} \), where \( h \) is the Planck’s constant. That is,
\[ L = n\hbar, \quad n = 1, 2, 3, \ldots \]  

(9.20)

In other words, the angular momentum is quantized.

2. Emission or absorption of radiation takes place when the electron makes a quantum leap from one stationary orbit to another. When the atom makes a transition from a higher energy state \( E_i \) to a lower energy state \( E_f \), Bohr proposed that the energy difference is radiated as a photon of frequency \( \nu \) with

\[ E_i - E_f = \hbar \nu \]

or

\[ \nu = \frac{E_i - E_f}{\hbar} \]  

(9.21)

This postulate is equivalent to Einstein’s postulate that the frequency of a photon of electromagnetic radiation is equal to the energy carried by the photon divided by Planck’s constant.

It is worthy of note that Bohr’s postulates mix both classical and non-classical physics. For example, the postulates assume the electron moving a round the nucleus in circular orbit obey classical mechanics, while the angular momentum is quantized.

We have earlier (Lecture 1) calculated the energies of the allowed states as

\[ E_n = \frac{Z^2 e^4 m}{8n^2 \hbar^2 \varepsilon_o^2} = -\frac{Z^2 \times 13.6eV}{n^2} \]  

(9.22)

For \( Z \) equal to one, and using equation (9.21) we obtain

\[ \nu = \frac{e^4 m}{2\hbar^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \langle n_i \rangle n_f \]  

(9.23)

This result agrees with the formulae given previously Balmer and others.

The Bohr’s model therefore predicts that

1) The normal state of an electron will be that state in which the electron has the lowest energy, i.e., state \( n = 1 \). This is called the ground state.

2) In an electric discharge, the atom receives energy due to collisions etc. This means that electrons must make transitions to a state of higher energy, or the excited state in which \( n > 1 \).
3) As in all physical systems, the atom will emit its excess energy and return to the ground state. This is achieved by a series of transitions in which the electron drops to excited states of successively lower energy eventually reaching the ground state. In every transition em radiation is emitted, the wavelength of which depends on the energy lost by the electron, i.e. on the initial and final quantum numbers.

4) Bohr’s model could explain the Balmer’s series and the other series.

It is important to point out however, that Bohr’s theory though successful, has limitations. There are some details of the spectrum it could not explain. For example, when the radiating atoms are placed in a magnetic field each energy level splits into a number of energy levels close to the main energy level. This causes the spectral line to split, a phenomenon known as the Zeeman effect, and which is explained only by the full quantum theory where four quantum numbers (the principal quantum number, \( n \), the orbital quantum number, \( l \), the magnetic quantum number, \( m \), the spin quantum number, \( m_s \)). Note that \( l \) can take the values 0,1,\ldots,n-1, \( m \) can take the values \(-l, -(l-1), \ldots, 0, \ldots, +l\), and \( m_s \) can take the values \( \pm \frac{1}{2} \).

![Figure 9.5 Energy levels of a hydrogen atom.](image-url)
Example  Helium has an ionization potential $(E_o = 24.6 \text{ eV})$, i.e. the ground state corresponding to energy $-24.6 \text{ eV}$. If there is an excitation level, $E_n$, of helium of $-21.4 \text{ eV}$. What is the frequency of the radiation emitted?

Solution  The frequency $\nu_n$ of the radiation emitted is obtained from the relation

$$\hbar \nu_n = E_n - E_o$$

$$\therefore \nu_n = \frac{[(-21.4) - (-24.6)] \times 1.6 \times 10^{19}}{6.6 \times 10^{-34}} \text{ Hz}$$

$$\therefore \lambda_n = \frac{c}{\nu_n} = \frac{3 \times 10^8 \times 6.6 \times 10^{-34}}{3.1 \times 1.6 \times 10^{-19}} = 3.9 \times 10^{-7} \text{ m}$$

9.3.2 The Wilson-Sommerfeld quantization rules

Despite the Bohr’s model success in explaining the observed spectral lines, it raised more questions; the main ones being the relation between Bohr’s quantization of angular momentum of an electron moving in a circular orbit, and the Planck’s quantization of the total energy of an entity such as an electron executing a simple harmonic motion (SHM).

Sommerfeld and Wilson gave a set of rules for the quantization of any physical system for which the coordinates are periodic functions of time, such that Bohr’s, and Planck’s quantization rules are just special cases. The set of rules can be state as follows:

For any physical system in which the coordinates are periodic functions of time, there exists a quantum condition for each coordinate. These quantum conditions are

$$\oint P_q dq = n_q \hbar$$

(9.24)

where $q$ is one of the coordinates, $P_q$ is the momentum associated with the coordinate, $n_q$ is the quantum number which takes on the integral values $\oint$ means the integration is taken over one period of the coordinate $q$.

For example, consider a 1-D simple harmonic oscillator. Its total energy in terms of position and momentum is

$$E = K + V = \frac{P_x^2}{2m} + \frac{kx^2}{2}$$

or
Equation (9.25) is that of an ellipse. A point at any instant of the oscillator is given by the coordinates $P_x$ and $x$. The 2-D space represented by the plane $P-q$ is known as the **phase space**; and the plot the phase diagram of the linear oscillator.

In one cycle of oscillation the point $(P_x, x)$ travel once around the ellipse. The semi-axes $a$ and $b$ of the ellipse \( \frac{P_x^2}{2mE} + \frac{x^2}{2E/k} = 1 \) are thus

\[
b = \sqrt{2mE}
\]

and

\[
a = \sqrt{2E/k}
\]
The area of the ellipse $= \pi ab = \int P_x dx$. Thus

$$\int P_x dx = \pi \sqrt{\frac{2mE}{k}} \sqrt{\frac{2E/k}{k/m}} = \frac{2\pi E}{\sqrt{k/m}},$$

but $\sqrt{\frac{k}{m}} = 2\pi v$, where $v$ is the frequency of the oscillator.

$$\therefore \int P_x dx = \frac{E}{v}.$$

Recall Eqn. (9.24). Thus

$$\int P_x dx = \frac{E}{v} = n_h = nh$$

or

$$E = nhv \equiv \text{the Planck's quantization law} \quad (9.26)$$

Note: The allowed states of oscillations are represented by a series of ellipses in the phase space, with the area enclosed between successive ellipses always being $\hbar$.

The Bohr’s quantization of angular momentum ($L = nh$) can be now obtained from equation (9.24) – the Wilson-Sommerfeld’s quantization rule thus:

$$\int P_y dq = n_q h$$

and

$$m\nu r = L$$

($\nu$ is velocity, $L$ is the angular momentum $= \text{constant}$).

The angular coordinate $= \theta$ and is a periodic function of time ($t$), that is, $\theta$ versus $t$ is a saw-tooth function that increases linearly from $\theta$ to $2\pi$ radians in one period, and thereafter repeats itself. Thus for the quantization rule we have

$$\int P_\theta dq = \int Ld\theta = nh$$

and

$$\int Ld\theta = \int_0^{2\pi} Ld\theta = nh$$
But $L = \text{constant.}$

\[ \therefore \int_{0}^{2\pi} Ld\theta = 2\pi L \]

\[ \therefore 2\pi L = nh \tag{9.27} \]

or

\[ L = \frac{nh}{2\pi} \equiv n\hbar \]

where $n = 1, 2, 3\ldots\ldots$. *Equation (9.27) is the Bohr’s quantization rule.*

We can rewrite the Bohr’s quantization rule

\[ mvr = Pr = \frac{nh}{2\pi}, n = 1, 2, 3, \ldots \]

where $P = \text{linear momentum of an electron in an allowed orbit of radius } r$.

### 9.3.3 The Correspondence Principle

We notice from Fig. 9.3 that the energy difference between one level and the next is very small for large values of the quantum number $n$. Similarly the difference between the radius of one Bohr orbit and the next is also very small. Therefore if an electron in a stationary state of very large $n$ were to jump, step-by-step, to the next lower states, then the steps in energy and radius are very small and will appear to proceed almost continuously. We have also noted that the difference in angular momentum between on state and the next has a fixed value $\hbar$, which does not become smaller for large values of $n$. Nevertheless, the changes in angular momentum will also appear to proceed almost continuously. *Under these conditions the electron will behave much as a classical particle-the effects of quantization being barely noticeable.*

These arguments show that in the limiting case of large quantum numbers there is concordance between classical and quantum mechanics. Bohr summarized this in his **Correspondence Principle**: *in the limiting case of large quantum numbers, the frequencies and the intensities of radiation calculated from classical theory must agree with those of quantum theory.*

### 9.4 Wave Mechanics

Sommerfeld’s elaboration of the Bohr’s quantum theory marked the highest level of classical mechanics, and its final decline. This is because Sommerfeld was able to calculate the spectrum of the hydrogen atom with very high accuracy but could do so for neither a hydrogen molecule nor a helium atom. *It is worth remembering that Bohr had used both classical and quantum theories.* Upon the discovery of the wave aspects of
electrons, it became necessary to abandon the classical concept of a particle, and also classical kinematics and dynamics and had to be replaced by a new concept of quantum-mechanical ‘particle’ whose state is described by a wave, and a new set of laws of wave mechanics. In this new concept, the classical mechanics turns out to be a special, limiting case.

9.4.1 de Broglie (Matter) Waves

It has already been noted that to explain some phenomena such as the photoelectric effect, the particle characteristics had to be assigned to electromagnetic radiation. It is further known that electromagnetic radiation behave like a wave, i.e., exhibits interference and diffraction. Hence electromagnetic radiation exhibits a wave-particle duality. In certain circumstances it behaves like a wave, while in other circumstances it acts as a particle. Note that a particle is localized while a wave spreads out and occupies a relatively large portion of space.

Louis de Broglie (1924) proposed that if em radiation exhibits wave-particle duality, then perhaps material objects such as electron may at times act like waves. This means that if a material object is passed through a slit whose aperture is comparable to the wavelength associated with them, they will undergo diffraction just as photons do in a single-slit experiment. De Broglie’s hypothesis is a statement about the grand symmetry of nature, which as we know comprises entirely of matter and radiation.

For a photon \( v = \frac{E}{h} \) and \( \lambda = \frac{h}{P} \) thus the corresponding de Broglie wavelength (a moving body is associated with de Broglie waves) is given by

\[
P = mv = \frac{h}{\lambda} \Rightarrow \lambda = \frac{h}{p} = \frac{h}{mv}
\]  
(9.28)

It is noted therefore that equation (9.28), the de Broglie’s relation, predicts the wavelength \( \lambda \) of matter associated with the motion of a material particle possessing momentum \( P \).

Examples:

1). What is the de Broglie wavelength of a ball of mass \( m = 1 \) kg, moving at a speed \( v = 10 \) ms\(^{-1}\)?

Solution:
\[ \lambda = \frac{h}{P} = \frac{h}{mv} = \frac{6.6 \times 10^{-34} J \cdot s}{1.0 kg \times 10 ms^{-1}} = 6.6 \times 10^{-25} \text{ m}. \] This wavelength is barely perceptible.

2). What is the de Broglie wavelength of an electron whose K.E. is 100eV?

**Solution:**

\[ \lambda = \frac{h}{P} = \frac{h}{\sqrt{2mK}} = \frac{6.6 \times 10^{-34} J \cdot s}{1.0 kg \times 100 ev \times 1.6 \times 10^{-19} Jm / ev} = \frac{6.6 \times 10^{-34} J \cdot s}{5.4 \times 10^{-24} kg \cdot ms^{-1}} = 1.2 \times 10^{-10} m \text{ or } 1.2 \text{ Å}. \]

Equation (9.28) and the above examples illustrate that there is no scale of size at which the wave-like property abruptly disappears. It shows that as the mass (and hence momentum \( P \)) becomes large, the wavelength \( \lambda \) becomes very small, and the length scale over which wave-like behaviour is discernable shrinks correspondingly. Thus for macroscopic objects the wavelength associated with them is so small that the wave-like aspects of matter are negligible, hence the unobserved matter waves in daily life. Note that it is the smallness of \( h \) that obscures the existence of matter waves in the macroscopic world.

In terms of the de Broglie wavelength (\( \lambda \)), the Bohr’s equation becomes

\[ \frac{hr}{\lambda} = \frac{nh}{2\pi} \text{ or } 2\pi n = \lambda \] (9.29)

Thus the allowed orbits are those in which the circumference of the orbit can contain exactly an integral number of de Broglie wavelengths (see Figs. 9.7 and 9.8).

Fig. 9.7 Allowed orbit which corresponds to a complete de Broglie wave joined on itself

Fig. 9.8 Prohibited orbit since the fractional number of wavelengths result in destructive interference
Frank and Hertz experimentally confirmed the quantization of integral energy states of an atom, as predicted by the Bohr’s theory experimentally in 1914. Thus this experiment provides

1. a direct method of showing the quantization of energy and,
2. a direct method for measurements of the energy difference between the quantum states of an atom.

Another experiment that confirmed the wave nature of matter is the Davison-Germer experiment. You can read about the experimental details of Frank and Hertz, and Davison-Germer in standard textbooks of Quantum Physics or Modern Physics.

9.4.2 The Wave-Particle duality and the Complementarity’s Principle

The wave-particle nature of matter is now accepted as valid, though in any given measurement only one model is applicable, i.e. both models (the wave model and wave model) are not used in the same circumstances. Neils Bohr summarized this situation in his principle of Complementarity. That is, the particle and wave models are complementary: if a measurement confirms the wave nature of radiation or matter, then it is impossible to prove the particle nature in the same experiment, and vice-versa.

9.4.3 The probability Interpretation of de Broglie Waves

You have learnt in the Waves and Optics course that in a double slit experiment with light, an interference pattern is obtained. According to the wave model, the intensity $I$ (energy per unit area per unit time) at a point on the screen is given by

$$ I = \varepsilon_0 c \varepsilon^2 $$

(9.30)

where $\varepsilon$ is the value of the electric field at a particular point, $\varepsilon_0$ is the permittivity of free space and $c$ the velocity of light.

According to the photon picture, on the other hand, the intensity at a point is given by

$$ I = h\nu N $$

(9.31)

where $N$ is the photon flux (number of photons per unit area per unit time) arriving at a particular point of the screen.

We cannot predict a priori where any individual photon will strike the screen, producing a flash. However, since the final pattern comprises alternating bright and dark bands, any photon has a high probability of striking a bright band a zero probability of arriving at a dark band. $N$ is thus a measure of the probability of finding a photon near a point.

From equations (9.30) and (9.31) it is noticed, $N \propto \varepsilon^2$. Thus in terms of the quantum interpretation of electromagnetic radiation, the quantity that is undergoing the oscillation,
namely the electric \( \epsilon \), is a function whose square is the probability of finding a photon at a given point.

The interference pattern described above could as well be produced by matter waves instead of the photons. Thus the probability interpretation given above can equally be applied to matter waves. Thus with matter waves, the quantity oscillating with the de Broglie wavelength \( \lambda = \frac{h}{mv} \) is that \textit{wave function} whose square gives the probability of finding a particle (e.g. an electron) at a given place. This \textit{wave function} is commonly denoted \( \psi \). That is, \( |\psi|^2 \) (or \( \psi^*\psi \) if \( \psi \) is complex) is the probability of finding a particle there at that time. \textbf{The integral of \( |\psi|^2 \) (known as the probability density) over all space must be finite if the particle is to be found somewhere.} If

\[
\int_{-\infty}^{\infty} |\psi|^2 dV = 1
\]

is zero, the particle does not exist, and if it is infinity, the particle exists everywhere simultaneously. Thus as long as \( |\psi|^2 \not\geq 0 \), there is some chance, however small, that the body may be detected there.

\[
\int_{-\infty}^{\infty} |\psi|^2 dV = 1 \tag{9.32}
\]

is mathematical statement that the particle exists somewhere. A wave function that obeys Eq. (9.32) is said to be \textit{normalized}.

\textbf{In order to reconcile the wave and particle pictures of matter, we must give up the notion of giving the location of a particle exactly.} Instead we talk of the probability of finding a particle at a particular location at a particular time.

\textbf{9.4.4 The Heisenberg Uncertainty (indeterminacy) Principle}

In general it states that \textit{it is impossible to know precisely the exact position of a particle and its momentum simultaneously.} When the position is measured the momentum is disturbed, and unlike in classical mechanics, this disturbance cannot be allowed for. Remember that in classical mechanics the equations of motion of a system with given forces can be solved to give us the position and momentum at all values of the time.

The uncertainties \( \Delta x \) and \( \Delta Px \) in position and momentum respectively are related by

\[
\Delta P_x \Delta x \geq \frac{\hbar}{2} \tag{9.33}
\]
From equation (9.33) if $\Delta x = 0$, i.e., if we know position exactly then $\Delta P_x = \infty$. The restriction is not on the accuracy of the measurement of position ($x$) or momentum ($P_x$), but on the product $\Delta P_x \Delta x$ in a simultaneous measurement of both.

The Heisenberg uncertainty principle can also be formulated in terms of other conjugate variables. For example the measurement of energy ($E$) and the time ($t$) required for the measurement. The uncertainties in energy and time $\Delta E$ and $\Delta t$ respectively are related by

$$\Delta E \Delta t \geq \frac{\hbar}{2} \tag{9.34}$$

Therefore the energy of a body can be known precisely ($\Delta E = 0$) only if the measurement is made over an infinite period of time ($\Delta t = \infty$).

The consequences of uncertainty principle are:

1. Since it is impossible in a single experiment to measure pairs of conjugate variables (e.g. $P_x$ and $x$, $E$ and $t$) to arbitrary precision therefore both the particle and the wave nature of matter cannot be measured in the same experiment. For example, a photon specified by a precise value of frequency $\nu$ has a precise momentum $P = h\nu / c$, so its position is completely indeterminate (i.e., it is not localized in space).

2. Since we cannot determinately predict both position and momentum simultaneously, we cannot specify the initial conditions of motion exactly; and hence cannot determine the future behaviour of the system. Instead, therefore, of making definite predictions, we can only state the possible results of an observation in probabilistic terms. That is, the results are stated in terms of their relative probabilities of occurrence.

3. A particle such as an electron cannot have a well-defined path through space-time since the concept of a trajectory implies that at a given instant, the position and velocity can both be specified.
SUMMARY

1. A black body is defined as one that absorbs all incident electromagnetic radiation.

2. Stefan’s law:  \[ E = \frac{4\delta}{c} T^4 \]

3. Wien’s displacement law:  \[ \lambda_{\text{max}} \propto \frac{1}{T} \text{ or } \lambda_{\text{max}} T = \text{ constant} \]

4. Raleigh-Jean’s formula:  \[ E(\lambda) d\lambda = \frac{8\pi}{\lambda^4} kTd\lambda \]

5. Planck’s hypothesis:  \[ E = h\nu = \hbar \omega \]

6. Average energy of a quantized oscillator is  \[ \bar{E} = \frac{h\nu}{e^{h\nu/kT} - 1} \]

7. Photoclectric effect is the ejection of electrons from the surface of a metal when a beam of monochromatic light of some frequency (\( \nu \)) is shone on the surface, and it takes place when  \( \hbar \omega = \Phi + T \)

8. Dulong-Petit law:  \[ C_v = \left( \frac{\partial E}{\partial T} \right)_v = 3Nk \]

9. Einstein’s relation for heat capacity:  \[ C_v = 3R\left( h\nu/kT \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)} \]

10. Rydberg’s formula:  \[ \frac{1}{\lambda} = R_n \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \]

11. Wilson-Sommerfeld’s quantization rules:  \[ \oint P_i dq = n_i \hbar \]

12. The de Broglie wavelength (a moving body is associated with de Broglie waves) is given by  \[ P = m\nu = \hbar \Rightarrow \lambda = \frac{\hbar}{P} = \frac{\hbar}{mv} \]

13. The Correspondence Principle: in the limiting case of large quantum numbers, the frequencies and the intensities of radiation calculated from classical theory must agree with those of quantum theory.

14. The Uncertainty Principle: It is impossible to know precisely the exact position of a particle and its momentum simultaneously, and is expressed by  \[ \Delta P_x \Delta x \geq \frac{\hbar}{2} \text{ or } \Delta E \Delta t \geq \frac{\hbar}{2} \]
EXERCISES

1. The element of an electric heater, with an output of 1.0 kW, is a cylinder 25 cm long and 1.5 cm diameter. Calculate the temperature when it is in use, if it behaves as a black body. (The Stefan’s constant = $5.7 \times 10^{-8}$ Wm$^{-2}$K$^{-4}$). (Ans: 1105 K).

2. Explain what is meant by (a) black-body (b) black-body radiation. Use the same axes sketch graphs, in one instance, to illustrate the energy distribution coming from a black body at (a) 1000 K, and (b) one at 2000 K.

3. In an experiment on photoelectric experiment a radiation of wavelength $4.00 \times 10^{-7}$ m was used and the maximum electron energy was found to be $1.40 \times 10^{-19}$ J. If the experiment was repeated but with a radiation of wavelength $3.00 \times 10^{-7}$ m the maximum energy was $3.06 \times 10^{-19}$ J. Derive the value for the Planck’s constant.

4. What is Photoelectric effect? Discuss how the observations of this effect support the quantum theory of electromagnetic radiation. Radiation of wavelength 180 nm ejects photoelectrons from the plate of potassium whose work function is 2.0 eV. What is the maximum energy of the emitted electrons? (Ans. $7.8 \times 10^{-19}$ J)

5. Describe the results obtained in experiments to investigate the variation of photoelectric emission as the frequency and intensity of the light is varied.

6. Light of a frequency $5.0 \times 10^{14}$ Hz liberates electrons with energy $2.31 \times 10^{-19}$ J from a certain metallic surface. What is the wavelength of UV light which liberates electrons of energy $8.93 \times 10^{-19}$ J? (Ans: $2.0 \times 10^{-7}$ m)

7. Explain why a glowing gas, for example neon in a decoration tube, gives only certain wavelengths of light?

8. What are the chief characteristics of a line spectrum? Explain how line spectra are used in analysis for identification of elements.

9. Find the wavelength of the photon emitted when a hydrogen atom goes from the n = 10 state to the ground state. (Ans. $920 \times 10^{-10}$ m).

10. If a golf ball of mass 0.05 kg is to have a de Broglie wavelength of 10-10 m, what would be its momentum and speed? Comment on these results. (Ans: $6.6 \times 10^{-24}$ kg.m/s, $1.3 \times 10^{-22}$ m/s).

11. If the uncertainty in the position of the ball described in question 10 was $10^{-10}$ m. What is the uncertainty in its momentum? Its speed? Comment on your results. (Ans: $\Delta P_x \approx 7 \times 10^{-24}$ kgm/s, $\Delta v \approx 1 \times 10^{-22}$ m/s).

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