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G. ARULDHAS

Origin of the Quantum Theory

1.1 LIMITATIONS OF CLASSICAL PHYSICS

The first scientific attempt to study the nature of light radiation was that of Sir Isaac Newton who proposed the corpuscular theory of light. According to this theory, light consists of tiny perfectly elastic particles, called *corpuscles* which travel in all directions in straight lines with the velocity of light. It could not explain phenomena such as interference, diffraction and polarization. It predicted that the velocity of light is more in a denser medium than that in a rarer medium.

The theory that light is propagated as a wave through a hypothetical elastic medium called *ether* was developed by Huygens, Young and Fresnel. They considered light as propagation of mechanical energy. It got established as it could explain most of the experimentally observed phenomena including the velocity of light in different media. A completely different concept regarding the nature of light was proposed by Maxwell in the second half of the nineteenth century. According to him, light consists of electromagnetic waves with their electric and magnetic fields in planes perpendicular to the direction of propagation. The electric and magnetic fields associated with the wave are governed by Maxwell's equations. Predictions of Maxwell were confirmed experimentally by Hertz. The electromagnetic theory of light was received well though it had failed to explain phenomena such as photoelectric effect and emission of light.

Thus, towards the end of the nineteenth century there was a sense of completion among the physicists as they thought that classical physics was capable of explaining all observable phenomena. Then came a series of important

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experimental discoveries starting with X-rays in 1895, radioactivity in 1896 and electron in 1897, which could not be explained, on the basis of classical physics. In addition, lot of experimental observations starting with black-body radiation and optical spectra accumulated could not be explained by the classical theory.

Black-body Radiation Curves

The spectral energy density u_v of black-body radiation from a black-body cavity depends only on frequency n and temperature T of the cavity. Based on thermodynamic arguments, Wien attempted to explain the observed spectral energy density verses frequency v curves. The agreement with experimental results was good only in the high-frequency region (Figure 1.1). Treating radiation inside a black body as standing electromagnetic waves, Rayleigh and Jeans estimated the number of modes of vibration per unit volume in the frequency range v and $v + dv$ and evaluated the spectral energy density u_v by taking its product with the average energy of an oscillator of frequency v. Their expression agreed with experiment only at low frequencies. The methods based on classical theories thus failed to give a single formula that could agree with the experimental black-body radiation curve for the entire frequency range. There is no wonder that this disagreement led to a complete revision of our ideas of physics.
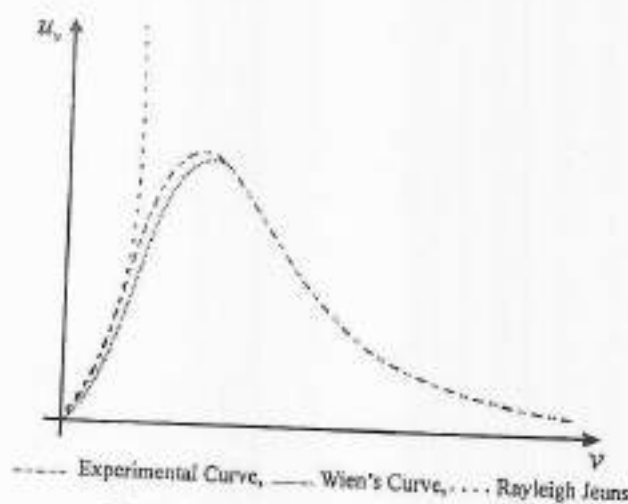

----- Experimental Curve, ——. Wien's Curve, ... Rayleigh Jeans

Figure 1.1   Black-body radiation curve.

Optical Spectra

Each chemical element showed characteristic emission spectrum consisting of discrete lines. Comparatively, simple spectrum was observed for hydrogen atom. In 1885, J.J. Balmer arranged them in the form of a series and had suggested the following empirical formula for the wavelength:

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \right.$$

where, R is the Rydberg constan were also discovered (Table 1.1)

$$\frac{1}{\lambda} =$$

where

$$m = 1, 2, 3, \cdots \quad n =$$

The regularities found in the spe general mechanism in the emissi give the correct mechanism respo

Table 1.1   The

Name of series	Lower state (
Lyman series	$m = 1$
Balmer series	$m = 2$
Paschen series	$m = 3$
Brackett series	$m = 4$
Pfund series	$m = 5$

Photoelectric Effect

When light is incident on certain These are called *photoelectrons* a *effect*. Some of the important conc of the phenomenon are listed belo

1. The energy distribution of intensity of the incident lig

2. The maximum kinetic energ is found to be proportional

3. For a given metal, photoelec incident light is below a certa of incident light.

4. For a given frequency, the n proportional to the intensity

5. There seems to be no time l resulting photocurrent.

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \qquad n = 3, 4, 5, \cdots \tag{1.1}$$

where, R is the Rydberg constant for hydrogen. Later, other spectral series were also discovered (Table 1.1) and they were found to obey the formula:

$$\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \tag{1.2a}$$

where

$$m = 1, 2, 3, \cdots \qquad n = (m + 1), (m + 2), (m + 3), \cdots \tag{1.2b}$$

The regularities found in the spectral lines indicate that there must be some general mechanism in the emission of light. The classical theories failed to give the correct mechanism responsible for the spectral series in hydrogen.

Table 1.1 The Hydrogen Spectral Series

Name of series	Quantum number		Region
	Lower state (m)	Upper state (n)	
Lyman series	$m = 1$	$n = 2, 3, 4, \cdots$	Ultraviolet
Balmer series	$m = 2$	$n = 3, 4, 5, \cdots$	Visible
Paschen series	$m = 3$	$n = 4, 5, 6, \cdots$	Infrared
Brackett series	$m = 4$	$n = 5, 6, 7, \cdots$	Infrared
Pfund series	$m = 5$	$n = 6, 7, 8, \cdots$	Infrared

Photoelectric Effect

When light is incident on certain metallic surfaces, electrons are released. These are called *photoelectrons* and the phenomenon is called *photoelectric effect*. Some of the important conclusions arrived from a detailed investigation of the phenomenon are listed below.

1. The energy distribution of the photoelectrons is independent of the intensity of the incident light.

2. The maximum kinetic energy of the photoelectrons from a given metal is found to be proportional to the frequency of the incident radiation.

3. For a given metal, photoelectrons are not emitted if the frequency of the incident light is below a certain threshold value, whatever be the intensity of incident light.

4. For a given frequency, the number of photoelectrons emitted is directly proportional to the intensity of incident light.

5. There seems to be no time lag between the onset of irradiation and the resulting photocurrent.

Though attempts were made to explain these aspects on the basis of classical ideas, the different conclusions stood unexplained.

Specific Heat of Solids

In solids, the atoms vibrate about their equilibrium positions in their lattice sites. Based on the law of equipartition of energy, the average energy of a simple harmonic oscillator is kT, where k is the Boltzmann constant and T is the absolute temperature. An atom can vibrate about three mutually perpendicular directions, the average energy of an atom is $3kT$. Then the energy per gram atom is $3NkT = 3RT$, N being the Avogadro's number and R, the gas constant. This leads to a value of $C_v = 3R$, which is known as the Dulong and Petit's law. At ordinary temperatures, solids generally obey this relation, which is based on classical theory. However, when the temperature is lowered the specific heat decreases and goes to zero when $T \rightarrow 0$ K. Thus, the classical ideas failed to explain the variation of specific heat of solids with temperatures.

Thus, by 1900 scientists were convinced that a number of experimentally observed phenomena could not be explained on the basis of classical physics and certain new revolutionary ideas are needed to understand things better.

1.2 PLANCK'S QUANTUM HYPOTHESIS

The problem that confronted Max Planck was a theoretical explanation for the black-body radiation curves. As already mentioned, the Wien's formula agreed well with experimental results at high frequencies whereas the one due to Rayleigh and Jeans agreed at low frequencies. In 1900, Planck modified Wien's formula in such a way that it fitted with the experimental curves precisely and then he looked for a sound theoretical basis for the formula. He assumed that the atoms of the walls of the black body behave like tiny electromagnetic oscillators each with a characteristic frequency of oscillation. The oscillators emit electromagnetic energy into the cavity and absorb electromagnetic energy from it. Planck then boldly put forth the following suggestions regarding the atomic oscillators:

1. An oscillator can have energies given by

$$E_n = nh\nu, \qquad n = 0, 1, 2, 3, \ldots \qquad (1.3)$$

where ν is the oscillator frequency and h is a constant known as *Planck's constant*. Its value is 6.626×10^{-34} Js. In other words, the oscillator energy is *quantized*.

2. Oscillators can absorb or emit energy only in discrete units called *quanta*. That is

$$\Delta E_n = \Delta n h \nu = h\nu \qquad (1.4)$$

An oscillator, in a quantized state, neither emits nor absorbs energy.

The average energy ε of canonical distribution formula:

$$\varepsilon = \sum_{n=?}^{?}$$

$$= \frac{\sum_{n=0}^{\infty}}{\sum_{n=?}^{?}}$$

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The quantization condition, E equipartition of energy which is number of oscillators per unit vo $(8\pi\nu^2/c^3)\, d\nu$. With the above e energy density u_ν is given by:

$$u_\nu = \frac{8\pi h}{c^3}$$

Equation (1.6) is the Planck's rad or Rayleigh–Jeans law according

$$\frac{h\nu}{kT} \gg$$

Planck's explanation of the b the crucial step in the development on a firm basis by the pioneering years. The concept that energy is c was reluctant to accept it. This ca attempts to fit the elementary quanti into the classical theory continued great deal of effort".

1.3 EINSTEIN'S THEORY C

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The average energy ε of an oscillator can be evaluated on the basis of canonical distribution formula:

$$\varepsilon = \frac{\sum_{n=0}^{\infty} \varepsilon_k \exp\left[-\varepsilon_n/(kT)\right]}{\sum_{n=0}^{\infty} \exp\left[-\varepsilon_n/(kT)\right]}$$

$$= \frac{\sum_{n=0}^{\infty} nh\nu \exp\left[-nh\nu/(kT)\right]}{\sum_{n=0}^{\infty} \exp\left[-nh\nu/(kT)\right]}$$

$$= \frac{h\nu}{\exp\left[h\nu/(kT)\right] - 1} \tag{1.5}$$

The quantization condition, Eq. (1.3), thus invalidates the theorem of equipartition of energy which is based on classical physics. It is known that the number of oscillators per unit volume in the frequency range ν and $\nu + d\nu$ is $(8\pi\nu^2/c^3)\, d\nu$. With the above expression for average energy ε, the spectral energy density u_ν is given by:

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{\exp\left[h\nu/(kT)\right] - 1} \tag{1.6}$$

Equation (1.6) is the Planck's radiation formula which reduces to the Wien's or Rayleigh–Jeans law according as

$$\frac{h\nu}{kT} \gg 1 \quad \text{or} \quad \frac{h\nu}{kT} \ll 1$$

Planck's explanation of the black-body radiation curves in 1900 provided the crucial step in the development of quantum ideas in physics which was put on a firm basis by the pioneering work of Einstein, Bohr and others in later years. The concept that energy is quantized was so radical that Planck himself was reluctant to accept it. This can be seen from his own words "my futile attempts to fit the elementary quantum of action (that is the quantity h) somehow into the classical theory continued for a number of years and they cost me a great deal of effort".

1.3 EINSTEIN'S THEORY OF PHOTOELECTRIC EFFECT

Einstein succeeded in explaining photoelectric effect on the basis of quantum ideas. He assumed that electromagnetic radiation travels through space in discrete quanta called *photons* as during the emission and absorption processes. The

energy of a photon of frequency ν is $h\nu$. When light photon of energy $h\nu$ is incident on a metallic surface, part of energy $h\nu_0$ is used to free the electron from the metallic surface and the other part appears as kinetic energy $\frac{1}{2}mv^2$ of the photoelectrons. The conservation of energy requires

$$h\nu = h\nu_0 + \frac{1}{2}mv^2 \qquad (1.7)$$

where $h\nu_0$, referred to as the *work function*, depends on the nature of the emitter. The frequency ν_0 is called the *threshold frequency*. This relation accounted for the experimental observations regarding photoelectric effect.

Though Planck quantized the energy of an oscillator, he believed that light travels through space as an electromagnetic wave. However, Einstein's photon hypothesis suggests that it travels through space not like a wave but like a particle. The photon hypothesis is thus in direct conflict with the wave theory of light. Millikan who verified Einstein's hypothesis calls it a 'bold, not to say reckless, hypothesis'.

In the photon picture, each photon transports a linear momentum $p = E/c$ $= h\nu/c$, where E is the photon energy. This conclusion can also be deduced from the theory of relativity. The relativistic expression for energy E is given by:

$$E^2 = c^2 p^2 + m_0^2 c^4$$

where c is the velocity of light and m_0 is the rest mass of the particle. Since the rest mass of the photon is zero,

$$E = cp \quad \text{or} \quad p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda} \qquad (1.8)$$

This equation contains in it both particle concept (E and p) and wave concept (ν and λ). Confirmation of particle nature of radiation was provided by Compton effect. Compton effect is discussed in the next section.

1.4 COMPTON EFFECT

The spectrum of X-rays scattered from a graphite block contains intensity peaks at two wavelengths, one at the same wavelength λ as the incident radiation and the other at a longer wavelength λ'. Assuming the incoming X-ray beam as an assembly of photons of energy hc/λ, Compton was able to show that

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_0 c}(1 - \cos\varphi) \qquad (1.9)$$

where m_0 is the rest mass of electron, c is the velocity of light and φ is the scattering angle. The factor $h/(m_0 c)$ is called the *Compton wavelength*. The Compton shift $\Delta\lambda$ varies between zero (for $\varphi = 0$, corresponding to a grazing collision) and $2h/(m_0 c)$ (for $\varphi = 180°$, corresponding to head-on collision).

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Agreement of Eq. (1.9) with the experimental results confirms the particle
nature of radiation.

1.5 QUANTUM THEORY OF SPECIFIC HEAT

Einstein explained the anomaly in the specific heat of solids using quantum
ideas. He replaced the $3N$ degrees of freedom of N atoms of the solid by $3N$
oscillators, all having the same frequency ν_E. Quantization of the energy of the
oscillators leads to the following expression for the vibrational specific heat

$$C_v = 3Nk\left(\frac{h\nu_E}{kT}\right)^2 \frac{\exp[h\nu_E/(kT)]}{\{\exp[h\nu_E/(kT)]-1\}^2}$$

$$= 3Nk\left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T)-1]^2} \tag{1.10}$$

where $\theta_E = h\nu_E/k$ defines the Einstein temperature. At ordinary temperatures
$T \gg \theta_E$, the expression for C_v approaches the Dulong and Petit law. At low
temperatures, $T \ll \theta_E$.

$$C_v = 3Nk\left(\frac{\theta_E}{T}\right)^2 \exp\left(-\frac{\theta_E}{T}\right) \tag{1.11}$$

which is not in agreement with the experimental T^3 dependence.

Debye improved the Einstein's model by assuming different frequencies
of vibration for the $3N$ oscillators and distributing them as in black-body
radiation. A cut-off frequency ν_D was also assumed. Debye derived the following
T^3 law for C_v when $h\nu_D/(kT) \gg 1$.

$$C_v = \frac{12\pi^4}{5} Nk\left(\frac{kT}{h\nu_D}\right)^3 \tag{1.12}$$

The agreement between the Debye model and the experimental observations is
good.

1.6 BOHR MODEL OF HYDROGEN ATOM

Rutherford, based on the results of α-scattering experiment, was the first to
propose the nuclear model of the atom. In this model, the positive charge is
confined to a very small sphere called the *nucleus* and the electrons move
around it. This model of the atom is highly unstable as a moving electric
charge radiates energy. Consequently, the electron in the Rutherford model of
the atom spirals into the nucleus. Moreover, it failed to explain the observed
sharp spectral lines of atoms. The concept of the nuclear model of the atom
was thus available for Bohr in 1913.

$$\frac{1}{\lambda} = A\left(\frac{1}{n_1} - \frac{1}{n^2}\right) \qquad n = 1, 2, 3, \dots$$

The emission spectral lines of hydrogen were grouped into several series which fit the empirical formula, Eq. (1.2). A theoretical explanation of the hydrogen spectrum, based on quantum ideas, was first formulated by N. Bohr in 1913. He based his arguments on two assumptions, now known as Bohr's postulates:

Postulate 1 An electron moves only in certain allowed circular orbits, which are stationary states in the sense that no radiation is emitted. The condition for such states is that the orbital angular momentum of the electron equals an integral multiple of $\hbar\,(=h/2\pi)$, called *modified Planck's constant*. Therefore,

$$mvr = n\hbar, \qquad n = 1, 2, 3, \dots \tag{1.13}$$

Postulate 2 Emission or absorption of radiation occurs only when the electron makes a transition from one stationary state to another. The radiation has a definite frequency v_{nm} given by the condition:

$$h v_{nm} = E_m - E_n \tag{1.14}$$

Consider a hydrogen atom in which the electron of mass m moves with velocity v in a circular orbit of radius r centred in its nucleus. For simplicity, the nucleus is assumed to be at rest. The Coulombic attraction between the electron and the proton provides the necessary centripetal force. That is

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{ke^2}{r^2} \tag{1.15}$$

In this expression e is the electronic charge measured in coulombs and ε_0 is a constant called the *permittivity of vacuum*. The experimental value of ε_0 is 8.854×10^{-12} $C^2N^{-1}m^{-2}$. For convenience, we have written

$$k = \frac{1}{4\pi\varepsilon_0} = 8.984 \times 10^9 \ Nm^2C^{-2} \tag{1.16}$$

The kinetic energy (T) of the electron is then given by

$$T = \frac{1}{2}mv^2 = \frac{ke^2}{2r} \tag{1.17}$$

From Eq. (1.13), the velocity of the electron in its nth orbit is

$$v_n = \frac{n\hbar}{mr} \tag{1.18}$$

Substituting this value of v_n in Eq. (1.15), we get

$$r_n = \frac{n^2\hbar^2}{kme^2} \tag{1.19}$$

The state for which n are called the *excited* the *Bohr radius* and in SI units, we

The potential energy

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$$E$$

Therefore,

$$E_n$$

Substituting the values

$$E_n = -\frac{1}{(4\pi\varepsilon_0}$$

Substitution of Eq. (1.22 when the electron drops

$$v_{nm} = \frac{}{}$$

For hydrogen like system

$$E_n = -\frac{Z^2k^2n}{2\hbar^2n}$$

where Z is the atomic num in explaining the spectru
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The state for which $n = 1$ is called the *ground state* while states for which $n > 1$ are called the *excited states*. The radius of the orbit in the ground state is called the *Bohr radius* and is usually denoted by a_0.

In SI units, we get

$$a_0 = \frac{4\pi\varepsilon_0 h^2}{me^2} = 0.53 \,\text{Å} \tag{1.20}$$

The potential energy $V(r)$ of the electron proton system is

$$V(r) = -\frac{ke^2}{r} \tag{1.21}$$

The total energy of the hydrogen atom in the nth state is

$$E_n = T + V = \frac{ke^2}{2r_n} - \frac{ke^2}{r_n} = -\frac{ke^2}{2r_n}$$

Therefore,

$$E_n = -\frac{k^2 me^4}{2h^2}\frac{1}{n^2}, \qquad n = 1, 2, 3, \ldots \tag{1.22}$$

Substituting the values of constants, we have

$$E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{me^4}{2h^2}\frac{1}{n^2} = -\frac{13.6}{n^2} \,\text{eV}, \qquad n = 1, 2, 3, \ldots \tag{1.23}$$

Substitution of Eq. (1.22) in Eq. (1.14) gives the frequency of the spectral line when the electron drops from the mth to nth state

$$\nu_{mn} = \frac{k^2 2\pi^2 me^4}{h^3}\left(\frac{1}{n^2} - \frac{1}{m^2}\right), \qquad m > n \geq 1 \tag{1.24}$$

For hydrogen like systems (He^+, Li^{+2}, Be^{+3}), the energy is given by

$$E_n = -\frac{Z^2 k^2 me^4}{2h^2 n^2} = -\frac{Z^2 me^4}{(4\pi\varepsilon_0)^2 2h^2 n^2}, \qquad n = 1, 2, 3, \ldots \tag{1.25}$$

where Z is the atomic number of the system. Bohr model was highly successful in explaining the spectrum of hydrogen and hydrogen like atoms.

Three electronic length scales used in numerical calculations are the Bohr radius a_0, Eq. (1.20); the Compton wavelength $\lambda_c = h/m_0 c$ and the **fine structure constant** α defined by

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 hc} = \frac{1}{137} \tag{1.25a}$$

Often the Bohr formula, Eq. (1.23) is expressed in terms of Rydberg constant R_H defined by

$$R_H = \frac{\mu e^4}{8\varepsilon_0^2 ch^3} \qquad (1.25b)$$

For solving numerical problems, often we require the following relations connecting these parameters:

$$a_0 = \frac{h}{\alpha mc} \quad \text{and} \quad R_H = \frac{\mu c \alpha^2}{2h} \qquad (1.25c)$$

The Rydberg constant for an atom with a nucleus of infinite mass is denoted by R_∞. Then in the expression for R_H, μ has to be replaced by m, the mass of electron.

1.7 EXISTENCE OF STATIONARY STATES

Einstein's photoelectric equation proved unambiguously that electromagnetic radiation interacts with matter like an assembly of discrete quanta of energy. In 1914, Franck and Hertz reported an ingenious experiment to prove that mechanical energy is also absorbed by atoms in discrete quanta.

The experimental set-up consists of an electrically heated filament (cathode) along the axis of a cylindrical grid which is surrounded by a collector (anode). The whole set-up is placed in a quartz chamber filled with mercury vapour; refer to Figure 1.2(a). Electrons from the filament are accelerated to the grid by a positive potential V_1. A small retarding potential V_2 ($V_2 \ll V_1$) between the grid and anode retards the accelerated electrons. The electrons collected by the anode give rise to a current which is measured by a micrometer. The plot of collector current verses the accelerating potential V_1 is shown as in Figure 1.2(b). When V_1 is increased from zero to a critical potential V_c, the accelerated electrons make only elastic collisions with the atoms of mercury. However, when $V_1 = V_c$, the electrons make inelastic collisions near the grid and give the entire kinetic energy to mercury atoms. After losing their energy, the electrons are unable to overcome the retarding potential V_2 leading to a sharp fall in current. Electrons which have not made inelastic collisions reach the anode giving a small current. The first drop occurs at 4.9 V and a spectral line appears simultaneously in the emission spectrum of the mercury vapour at 253.6 nm, the value corresponding to a photon energy of 4.9 eV.

When the potential is increased further, the region where the electrons reach the critical energy of 4.9 eV moves closer to the filament. After losing the energy to mercury vapour by inelastic collision, the electron picks up energy on their way to the grid resulting in an increase of current. A second inelastic collision occurs near the grid, when $V_1 \cong 2V_c$ and a second current

Figure 1.2 (a)
(b) Plot of

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1.8 WILSON-SOM[...]

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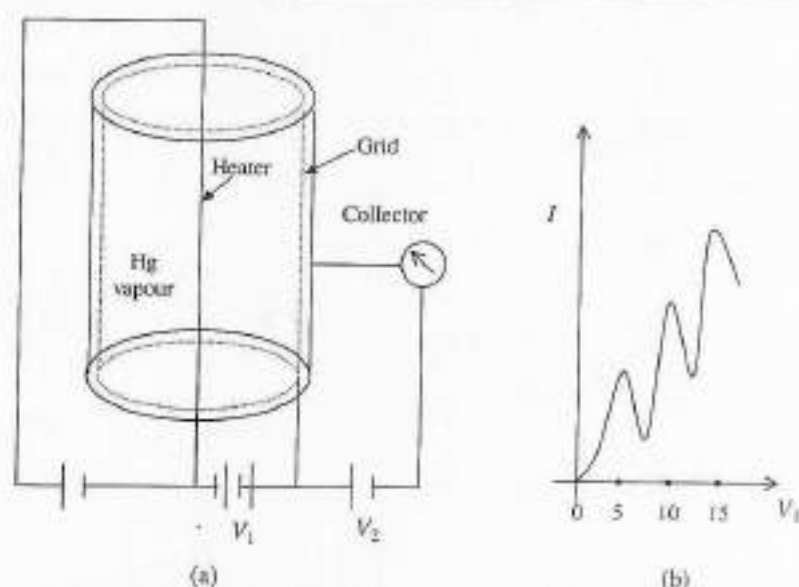of current. A second
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Figure 1.2   (a) Experimental arrangement of Franck and Hertz,
(b) Plot of collector current verses accelerating voltage.

minimum occurs as shown in Figure 1.2(b). A similar behaviour is found at
integral multiples of V_c. That is, the mercury atoms absorb mechanical energy
in quanta of 4.9 eV. Thus, the occurrence or minima in the I verses V_1 curve
can be explained only by the existence of stationary states in the atom.

1.8   WILSON–SOMMERFELD QUANTIZATION RULE

In 1915, Wilson and Sommerfeld proposed independently a more general
quantization rule in which the Hamilton's equations of motion are first solved
in the independent variables $q_1, q_2, \dots, q_n$ and $p_1, p_2, \dots, p_n$. The stationary
states are those for which the action integral of any periodic motion equals an
integer times h.

$$\oint p_i \, dq_i = n_i h, \qquad n_i = 0, 1, 2, \dots, n \qquad (1.26)$$

where the integration $\oint$ is over one cycle of motion. In circular orbits, the
orbital angular momentum $L = mvr$ is a constant of motion. Hence for circular
orbits Eq. (1.26) reduces to

$$\oint mvr \, d\phi = nh \quad \text{or} \quad mvr = \frac{nh}{2\pi} \qquad (1.27)$$

which is Bohr's quantization rule, Eq. (1.13). In the following sections, we
shall apply the general quantization rule to some cases of interest.

1.9 ELLIPTIC ORBITS OF HYDROGEN ATOM

The simplest force that is associated with point particles is the mutual central force acting along the line joining the two. Consider the two particles of the hydrogen atom with the nucleus of charge Ze fixed at the origin and the electron of mass m moving relative to the nucleus (refer to Figure 1.3). As per classical mechanics, the first integrals of the equations of motion of the system are

and

$$mr^2\dot{\theta} = L \quad \text{(a constant)} \tag{1.28}$$

$$\frac{1}{2}m\dot{r}^2 + \frac{L^2}{2mr^2} + V(r) = E \quad \text{(a constant)} \tag{1.29}$$
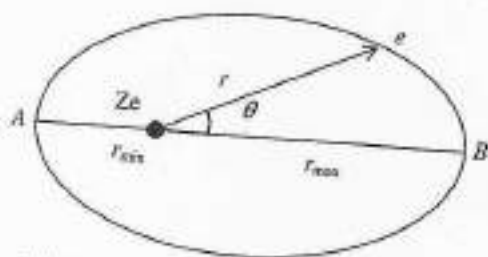

Figure 1.3 Parameters of the ellipse.

where

$$V(r) = -\frac{ke^2}{r} \tag{1.30}$$

L and E are the angular momentum and total energy of the system respectively. The radial momentum $p_r = m\dot{r}$ and the angular momentum $L = p_\theta$ obey the quantization rules;

$$\oint p_\theta \, d\theta = kh \quad \text{and} \quad \oint p_r \, dr = n_r h \tag{1.31}$$

where k and n_r are integers. Since p_θ is constant,

$$p_\theta \oint d\theta = kh \quad \text{or} \quad p_\theta 2\pi = 2\pi L = kh \tag{1.32}$$

From Eq. (1.29), we have

$$p_r = m\dot{r} = \pm\sqrt{2m\left(E + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{L^2}{2mr^2}\right)} \tag{1.33}$$

The positive value of p_r corresponds to the increase of r from r_{min} to r_{max} and the negative value to the other half of the elliptical path. Therefore,
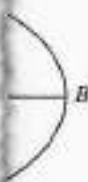
$$\oint p_r\, dr = 2\int_{r_{min}}^{r_{max}} \sqrt{2m\left(E + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{L^2}{2mr^2}\right)}\, dr = 2\pi\left(e^2\sqrt{\frac{m}{-2E}} - L\right)$$

Combining this result with Eqs. (1.31) and (1.32), we get

$$\frac{2\pi e^2}{4\pi\varepsilon_0}\sqrt{\frac{m}{-2E}} = (k + n_r)h = nh \tag{1.34}$$

where the principal quantum number, $n = n_r + k$. Solving for E, we have

$$E = -\frac{k^2 m e^4}{2\hbar^2 n^2} = -\frac{m e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2}, \qquad n = 1, 2, 3, \dots \tag{1.35}$$

which is same as Eq. (1.22). It may be mentioned here that no restriction is made to circular orbits while deriving Eq. (1.35).

At points A and B, $\dfrac{dr}{dt} = 0$ and this happens for $r = r_{min}$ and $r = r_{max}$.

When $\dfrac{dr}{dt} = 0$, from Eq. (1.33), we get

$$r^2 + \frac{e^2 r}{4\pi\varepsilon_0 E} - \frac{L^2}{2mE} = 0 \tag{1.36}$$

and the sum of the roots of this equation is given by

$$r_{min} + r_{max} = -\frac{e^2}{4\pi\varepsilon_0 E}$$

As $r_{min} + r_{max} = 2a$, the semi-major axis of the ellipse is

$$a = -\frac{e^2}{(4\pi\varepsilon_0)2E} \tag{1.37}$$

Substitution of the value of E gives a_n, the length of the semi-major axis of the nth orbit

$$a_n = \frac{4\pi\varepsilon_0 n^2 \hbar^2}{me^2} = n^2 a_0 \tag{1.38}$$

where a_0 is the Bohr radius.

Elliptic orbits of hydrogen atom was first solved by Sommerfeld as an example of the general quantization rule! The energy is dependent on the principal quantum number n which is the sum of k and n_r. Therefore, all orbits for which $k + n_r = n$ has the same value, will have the same energy. States of motion corresponding to the same energy are said to be *degenerate*. Among all

orbits having the same value of n, one will be a circular one for which $n_r = 0$, $k = n$. This explains why the energy expression is the same as the one by Bohr's theory for circular orbits. The case $k = 0$ was ruled out by Sommerfeld as it corresponds to motion of the electron along a straight line through the nucleus. Electron orbits for $n = 1, 2, 3$ are shown in Figure 1.4.
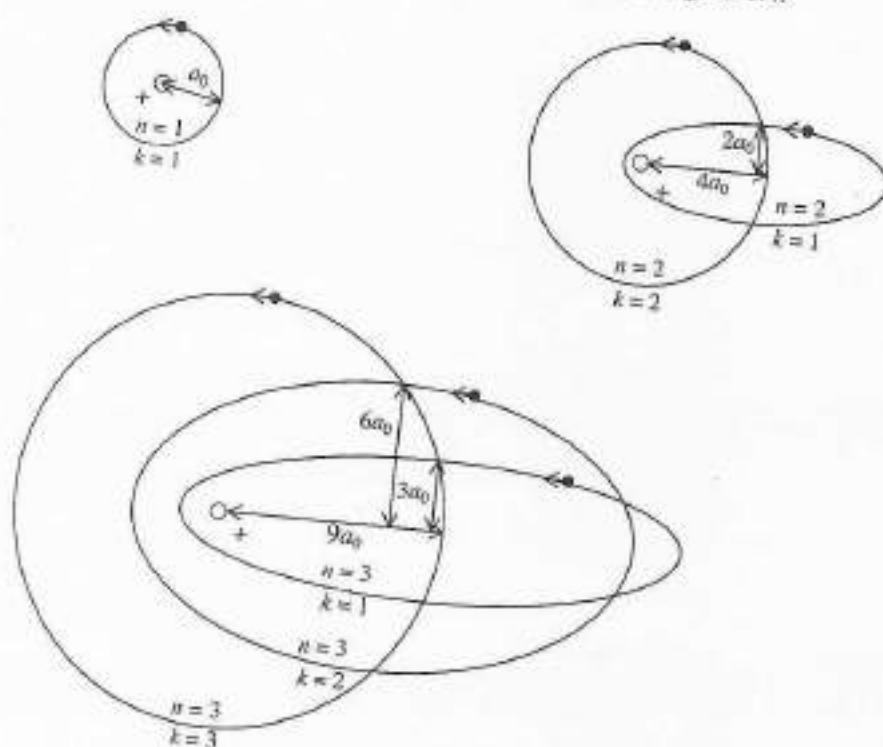

Figure 1.4 Sommerfeld electron orbits for $n = 1, 2, 3$.

1.10 THE HARMONIC OSCILLATOR

The displacement x with time t of a harmonic oscillator of frequency v_0 is given by

$$x = x_0 \sin (2\pi v_0 t)$$ (1.39)

The force constant k and frequency v_0 are related by the expression:

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \text{or} \quad k = 4\pi^2 m v_0^2$$ (1.40)

Therefore, the potential energy is

$$V = \frac{1}{2} k x^2 = 2\pi^2 m v_0^2 x_0^2 \sin^2(2\pi v_0 t)$$

The kinetic energy is

$$T = \frac{1}{2}$$

And the total energy is

According to the quantiza

$$\oint p_x$$

When x completes one cycl the values of dx/dt and dx

$$4\pi^2 m v_0^2 x_0^2 \int_0^{v_0} c($$

On solving, we get

$$2\pi^2 m v_0 x_0^2$$

Substituting the value of x_0

$$E_n = nh v$$

That is, according to old qua oscillator are integral multiple

1.11 THE RIGID ROTAT

A *rigid rotator* consists of tw the rotator is rigid, potential er in a plane is described by an a the angle coordinate $p_\theta = I \dot\theta$ constant of motion. The quanti

$$\int_0^{2\pi} p_\theta \, d\theta = Jh$$

That is, the angular momentum value of $p_\theta = I\omega$ the energy of

$$E_J = \frac{J^2}{8\pi}$$

The kinetic energy is

$$T = \frac{1}{2} m \left(\frac{dx}{dt} \right)^2 = 2\pi^2 m v_0^2 x_0^2 \cos^2(2\pi v_0 t)$$

And the total energy is

$$E = T + V = 2\pi^2 m v_0^2 x_0^2 \tag{1.41}$$

According to the quantization rule

$$\oint p_x \, dx = nh \quad \text{or} \quad m \oint \frac{dx}{dt} \, dx = nh \tag{1.42}$$

When x completes one cycle, t changes by period $T = 1/v_0$. Hence, substituting the values of dx/dt and dx, we get

$$4\pi^2 m v_0^2 x_0^2 \int_0^{1/v_0} \cos^2(2\pi v_0 t) \, dt = nh, \qquad n = 0, 1, 2, \dots$$

On solving, we get

$$2\pi^2 m v_0 x_0^2 = nh \quad \text{or} \quad x_0 = \left(\frac{nh}{2\pi^2 m v_0} \right)^{1/2} \tag{1.43}$$

Substituting the value of x_0 in Eq. (1.41), we have

$$E_n = nh v_0 = n\hbar\omega, \qquad n = 0, 1, 2, \dots \tag{1.44}$$

That is, according to old quantum theory, the energies of a linear harmonic oscillator are integral multiples of $h v_0 = \hbar\omega$.

1.11 THE RIGID ROTATOR

A *rigid rotator* consists of two mass points connected by a massless rod. As the rotator is rigid, potential energy is zero. A rigid rotator restricted to move in a plane is described by an angle coordinate θ. The momentum conjugate to the angle coordinate $p_\theta = I\dot{\theta} = I\omega$, where I is the moment of inertia, is a constant of motion. The quantization rule reduces to

$$\int_0^{2\pi} p_\theta \, d\theta = Jh \quad \text{or} \quad p_\theta = \frac{Jh}{2\pi}, \qquad J = 0, 1, 2, \dots \tag{1.45}$$

That is, the angular momentum p_θ is an integral multiple of $h/2\pi$. With this value of $p_\theta = I\omega$ the energy of a classical rotator $E = I\omega^2/2$ reduces to

$$E_J = \frac{J^2 h^2}{8\pi^2 I}, \qquad J = 0, 1, 2, \dots \tag{1.46}$$

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To describe a rigid rotator in space, one requires the two coordinates θ and ϕ of the polar coordinates. Application of the quantization rule gives the same expression as the one in Eq. (1.45) for the total angular momentum and

$$P_\phi = \frac{mh}{2\pi}, \qquad m = -J, -J+1, ..., J-1, J \tag{1.47}$$

for the component of angular momentum along the z-axis. The energy is independent of the quantum number m and is given by Eq. (1.46). Each energy level is $(2J + 1)$ fold degenerate.

1.12 PARTICLE IN A BOX

Consider a particle of mass m moving inside a rectangular box of sides a, b and c without the influence of any force. Let us assume that the collision with the walls of the box is perfectly elastic. The cartesian axes are taken along the edges of the box. The linear momentum p_x, p_y and p_z are constants of motion and change sign during collision with the walls. Applying the rule of quantization:

$$\oint p_x \, dx = 2ap_x = n_x h$$

We get

$$p_x = \frac{n_x h}{2a}, \qquad n_x = 0, 1, 2, ...$$

Similarly,

$$p_y = \frac{n_y h}{2b}, \qquad n_y = 0, 1, 2, ...$$

and

$$p_z = \frac{n_z h}{2c}, \qquad n_z = 0, 1, 2, ...$$

The total energy

$$E_{n_x, n_y, n_z} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{1.48}$$

In the case of a cubical box of side a

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{1.49}$$

The energy of the system is thus quantized.

1.13 THE CORRESPONDENCE PRINCIPLE

The *correspondence principle* of Bohr states that the quantum physics reduces to classical physics at large quantum numbers. To explain the principle, Bohr used a simple illustration based on the line spectra of one electron atom.

Classically, during the periodic motion in a stationary orbit, the frequency of the light emitted by the atom is equal to its frequency of revolution v_r. From Eqs. (1.17) and (1.18), we get

$$v_r = \frac{v_n}{2\pi r_n} = \frac{me^4}{(4\pi\varepsilon_0)^2 2\pi n^3 \hbar^3} \tag{1.50}$$

For the transition $(n + 1) \to n$, the frequency of the emitted radiation (v) is given by Eq. (1.24) as

$$v = \frac{2\pi^2 me^4}{(4\pi\varepsilon_0)^2 h^3}\left[\frac{1}{n^2} - \frac{1}{(n+1)^2}\right] = \frac{2\pi^2 me^4}{(4\pi\varepsilon_0)^2 h^3}\left[\frac{2n+1}{n^2(n+1)^2}\right] \tag{1.51}$$

It is clear that $v \to v_r$, when $n \to \infty$, as required by the correspondence principle.

1.14 THE STERN-GERLACH EXPERIMENT

The concept of vector atom model was introduced to explain certain experimental observations in the atomic spectra of complex atoms. This atom model has the two special features: *spatial quantization* and the *electron spin*. Direct experimental confirmation of these features was provided by the Stern-Gerlach experiment.

The magnetic moment μ of an atom arises due to orbital and spin motions of the electrons. In a uniform magnetic field, the magnetic moment vector experiences a torque which tends to turn the direction of μ and hence that of angular momentum with the magnetic field. This makes the vector μ to precess around the field keeping a fixed angle θ with the field. If the magnetic field is nonuniform, the atom with the magnetic moment experiences an additional translatory motion. Hence, if an atom with a magnetic moment is shot in the x-direction through a magnetic field which increases along the z-axis, it will be deflected in the positive or negative z-direction. The shift will depend on the value of μ_z. If μ_z takes continuous values the beam would spread out into a continuous band in the xz-plane. Instead, if there is space quantization each atom will enter the magnetic field in a particular quantum state defined with the magnetic field direction as the axis. Consequently, the beam will split into separate beams and produce a series of distinct spots or sharp lines, one for each possible value of μ_z.

In their experiment, Stern and Gerlach passed a collimated beam of silver atoms through an inhomogeneous magnetic field produced by a specially

designed electromagnet (Figure 1.5). While passing through the magnetic field, the beam splits into two parts, one travelling upwards and the other downwards, producing two spots on the screen.
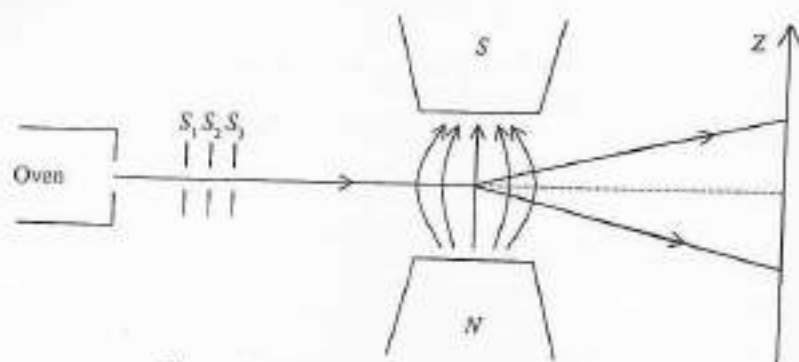
Figure 1.5 The Stern–Gerlach experiment.

In the ground state, the outer electron of silver atom is in an s-state ($5s$). Therefore, it has no orbital angular momentum and consequently no orbital magnetic moment. The observation of 2 spots suggests that all electrons have an intrinsic magnetic moment of the same magnitude with two possible orientations—parallel or antiparallel to the magnetic field. The origin of this magnetic moment can be understood if it is assumed that the electron of the silver atom has an intrinsic spin angular momentum. If the spin of the electron is s, the z-component of spin can have $2s + 1$ orientations. As two spots have been observed experimentally $2s + 1 = 2$ or $s = 1/2$. That is, the spin of electron is 1/2. Thus, spin, first detected in the Stern-Gerlach experiment, has become an 'observable'.

1.15 INADEQUACY OF QUANTUM THEORY

The quantum theory developed by Max Planck, Einstein and Bohr was found to be adequate in explaining certain phenomena such as black-body radiation, photoelectric effect, harmonic oscillator, rigid rotator, spectral lines of hydrogen atom, etc. However, it was inadequate to explain number of cases. Some of them are:

1. The general quantization rule is valid only for periodic systems. Hence the quantum theory is not applicable to non-periodic cases.

2. Even in the case of hydrogen spectrum, the theory could explain only the broad features.

3. Application of the quantum theory to helium atom, hydrogen molecule, etc., led to results contrary to experiments.

4. Failed to account the concept of half odd integer quantum numbers which are necessary for explaining Zeeman effect and fine structure of

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spectral lines. In other words, it failed to account for the concept of spin.

5. It failed to give a method for evaluating transition probabilities and intensities of spectral lines.

6. The theory was unsuccessful in explaining the dispersion of light.

These shortcomings suggest that the quantum theory is not a very general one and the defects cannot be removed by extensions and modifications. Therefore, one has to look for a more basic theory to account for all phenomena.

WORKED EXAMPLES

EXAMPLE 1.1 The work function of barium and tungsten are 2.5 eV and 4.2 eV, respectively. Check whether these materials are useful in a photocell, which is to be used to detect visible light.

Wavelength (λ) of visible light is in the range 4000–7000Å.

$$\text{Energy of 4000-Å light} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10} \times 1.6 \times 10^{-19}}$$
$$= 3.106 \text{ eV}$$

and

$$\text{Energy of 7000-Å light} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{7000 \times 10^{-10} \times 1.6 \times 10^{-19}} = 1.77 \text{ eV}$$

The work function of tungsten is 4.2 eV which is more than the energy range of visible light. Hence barium is the only material useful for the purpose.

EXAMPLE 1.2 Verify Eq.(1.23) for the energy of the hydrogen atom in the nth state.

From Eq. (1.23), we have

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -\frac{(9.11 \times 10^{-31}\text{ kg})(1.6 \times 10^{-19}\text{C})^4}{8(8.85 \times 10^{-12}\text{C}^2\text{N}^{-1}\text{m}^{-2})^2(6.626 \times 10^{-34}\text{Js})^2 n^2}$$

$$= -\frac{21.703 \times 10^{-19}}{n^2}\text{ J}$$

$$= -\frac{21.703 \times 10^{-19}\text{ J}}{(1.6 \times 10^{-19}\text{ J/eV})\, n^2}$$

$$= -\frac{13.56}{n^2}\text{ eV}$$

$$= 2.42 \times 10^{-12} \text{ m}$$
$$= 0.024 \text{ Å}$$

EXAMPLE 1.9 From a sodium surface, light of wavelength 3125Å and 3650 Å causes emission of electrons whose maximum kinetic energy is 2.128 eV and 1.595 eV, respectively. Estimate Planck's constant and work function of sodium.

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + \text{kinetic energy}$$

$$\frac{hc}{3125 \times 10^{-10}} = \frac{hc}{\lambda_0} + 2.128 \times 1.6 \times 10^{-19}$$

$$\frac{hc}{3650 \times 10^{-10}} = \frac{hc}{\lambda_0} + 1.595 \times 1.6 \times 10^{-19}$$

$$\frac{hc}{10^{-10}} \left(\frac{1}{3125} - \frac{1}{3650} \right) = 0.533 \times 1.6 \times 10^{-19}$$

Therefore,

$$h = \frac{0.533 \times 1.6 \times 10^{-19} \times 10^{-10} \times 3125 \times 3650}{525 \times 3 \times 10^8} = 6.176 \times 10^{-34} \text{ Js}$$

From the first equation, the work function

$$\frac{hc}{\lambda_0} = \frac{6.176 \times 10^{-34} \times 3 \times 10^8}{3125 \times 10^{-10}} - 2.128 \times 1.6 \times 10^{-19}$$

$$= 2.524 \times 1.6 \times 10^{-19} \text{ J}$$

$$= 2.524 \text{ eV}$$

REVIEW QUESTIONS

1. How classical physics failed to account for the spectral distribution of energy density in a black body?

2. Explain photoelectric effect. Define the terms: work function, threshold frequency and cut-off wavelength.

3. Briefly outline the mechanism by which photoelectrons are emitted.

4. List out the basic experimental results of the photoelectric phenomena.

5. Write the expression for the velocity of photoelectrons emitted when radiation of wavelength λ is incident on a photosensitive surface, the threshold wavelength being λ_0.

6. What is Compton effect? Explain its significance.

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7. Explain the assumptions of Planck with regard to cavity radiation and of Einstein with regard to photoelectric effect.

8. How particle nature of radiation was confirmed by the photoelectric effect and Compton effect?

9. Explain the postulates of Bohr with regard to hydrogen atom.

10. Apply Bohr's theory to singly-ionized helium atom. What relationship exists between this spectrum and the hydrogen spectrum?

11. Can a hydrogen atom absorb a photon whose energy exceeds its binding energy?

12. What are the different possibilities of spectral line emission for the hydrogen atom when the electron is excited to the $n = 5$ state?

13. State and explain the general quantization rule. Explain how it leads to Bohr's postulate regarding stationary states.

14. Sketch Sommerfeld electron orbits for $n = 4$.

15. Explain the significance of Stern–Gerlach experiment.

PROBLEMS

1. Light of wavelength 2000 Å falls on a metallic surface. If the work function of the surface is 4.2 eV, what is the kinetic energy of the fastest photoelectrons emitted? Also, calculate the stopping potential and threshold wavelength for the metal.

2. What is the work function of a metal, if the threshold wavelength for it is 580 nm? If light of 475 nm wavelength falls on the metal, what is its stopping potential?

3. How much energy is required to remove an electron from the $n = 8$ state of a hydrogen atom?

4. Calculate the frequency of the radiation that just ionizes a normal hydrogen atom.

5. A photon of wavelength 4 Å strikes an electron at rest and scattered at an angle of 150° to its original direction. Find the wavelength of the photon after collision.

6. When radiation of wavelength 1500 Å is incident on a photocell, electrons are emitted. If the stopping potential is 4.4 volts, calculate the work function, threshold frequency and threshold wavelength.

7. If a photon has wavelength equal to the Compton wavelength of the particle, show that the photon's energy is equal to the rest energy of the particle.

8. X-rays of wavelength 1.4 Å are scattered from a block of carbon. What will be the wavelength of scattered X-rays at (i) 180°, (ii) 90°, (iii) 0°?

2

Wave Mechanical Concepts

2.1 WAVE NATURE OF PARTICLES

The theory that radiation travels in space in the form of waves got established as it successfully explained the optical phenomena like reflection, refraction, interference, diffraction and polarization. However, to explain photoelectric effect and Compton effect one needs the particle or corpuscular nature of radiation. Thus, radiation possesses wave-particle duality. Sometimes it behaves like a wave and at times like a particle.

Matter Waves

The dual nature of radiation prompted Louis de Broglie to extend it to material particles also. He reasoned that (i) nature is strikingly symmetric in many ways, (ii) our observable universe is composed entirely of radiation and matter, (iii) if light has a dual nature, perhaps matter has also. Since matter is composed of particles, his reasoning suggested that one should look for a wave-like behaviour for matter. In other words, de Broglie assumed that a wave is associated with a particle in motion, called *matter wave*, which may be regarded as localized with the particle. Again he suggested that the wavelength of matter wave be given by the same relationship, namely

$$\lambda = \frac{h}{p} = \frac{h}{mv} \tag{2.1}$$

where m is the mass and v is the velocity of the particle. This relation is often referred to as the *de Broglie relation*.

Electron Diffraction Experiment

The concept of wave nature of material particles was independently tested by Davisson and Germer and by G.P. Thomson. Thomson's experimental arrangement is analogous to Laue's X-ray diffraction method. The arrangement as shown in Figure 2.1(a) consists of a discharge tube in which a beam of electrons from a cathode C is accelerated by a potential difference ranging from 10,000 to 50,000 volts. The electrons collimated by the tube A fall on a thin gold film of thickness of the order of 10^{-6} cm. The apparatus is evacuated to avoid collision of electrons with the molecules of the gas. The diffracted beam is allowed to fall on a fluorescent screen S or on a photographic plate P. The photograph of the diffracted beam has a system of concentric rings, as shown in Figure 2.1(b). Measuring the radii of the rings and the distance between the film and photographic plate, the angle of diffraction θ can be obtained. Knowing the distance between atomic planes d, the wavelength of the diffracted beam can be calculated. The experiment clearly demonstrates the wave nature of electron as diffraction pattern can only be produced by waves.
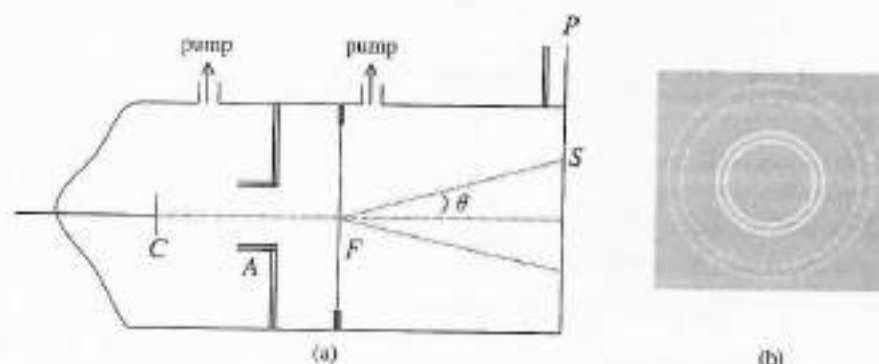
Figure 2.1 (a) Thomson's apparatus for electron diffraction, (b) diffraction pattern of a beam of electrons by thin gold foil.

In the acceleration process the electron behaves like a particle, in the diffraction process it behaves like a wave and in the detector it behaves like a particle. The electron which showed wave aspect in one part of the experiment showed particle aspect in two other parts of the same experiment. That is, for a complete description of physical phenomena, both particle and wave aspects of material particles are required. Hence, the new theory which we are looking for must account for the dual nature of radiation and matter.

Standing Wave of an Electron in the Orbit

An electron orbiting around a nucleus at a distance r is a bounded one and therefore the motion is represented by a standing wave. Only certain definite number of wavelengths can now exist in an orbit, otherwise the wave after

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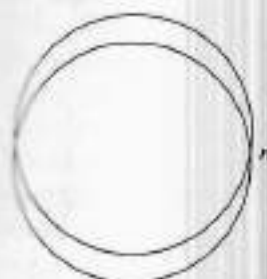quantization rule in a refine
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Figure 2.2 Standing

2.2 THE UNCERTAINTY

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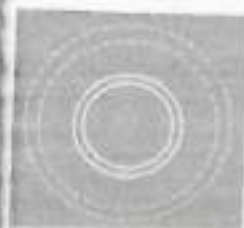
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..thematically,

$$\oint \frac{ds}{\lambda} = n, \qquad n = 1, 2, \ldots \tag{2.2}$$

..here the integration is over one complete revolution. Substituting $\lambda = h/(mv)$,
.. (2.2) reduces to

$$\oint mv\, ds = nh, \qquad n = 1, 2, \ldots \tag{2.3}$$

..hich is a form of the *general quantization rule*. For circular orbits, $ds = r\, d\theta$.

$$mvr \oint d\theta = nh \quad \text{or} \quad mvr = \frac{nh}{2\pi}, \qquad n = 1, 2, \ldots \tag{2.4}$$

..hich is *Bohr's quantization rule*. Thus, the de Broglie relation gives the
..uantization rule in a refined way which was earlier introduced as an ad hoc
..ypothesis. The standing wave patterns of the electron in an orbit are illustrated
.. Figure 2.2.
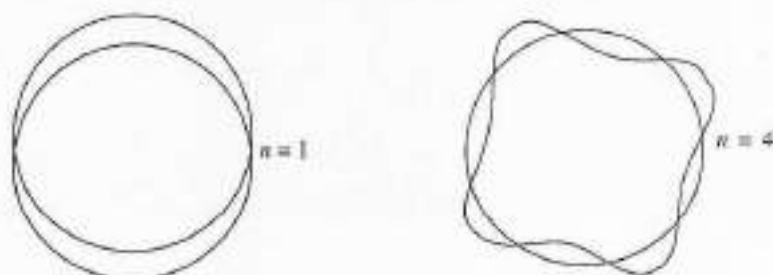
Figure 2.2 Standing wave patterns of an electron in an orbit for
$n = 1$ and $n = 4$.

2.2 THE UNCERTAINTY PRINCIPLE

As per classical ideas, it is possible to determine all dynamical variables of a
system to any desired degree of accuracy. This principle of determinism is the
backbone of classical physics.

Position-momentum Uncertainty

The position of a plane wave is completely indeterminate as it is of infinite
extent. Therefore, when waves are assigned to particles in motion an
indeterminacy arises automatically in the formalism because an electron wave
of definite frequency is not localized. Heisenberg analysed this indeterminacy
and proposed that no two canonically conjugate quantities can be measured
simultaneously. For the canonically conjugate variables x and p_x, mathematically,
the principle is stated as

$$\Delta x \, \Delta p_x \cong h \tag{2.5}$$

The uncertainty relation can be illustrated by the *single-slit experiment* discussed below.

Single-slit experiment. Consider a beam of monoenergetic electrons of speed v_0 moving along the y-axis. Let us try to measure the position x of an electron and its velocity component v_x in the vertical direction (x-axis). To measure x, we insert a screen S_1 which has a slit of width Δx (Figure 2.3). If an electron passes through this slit, its vertical position is known to this accuracy. This can be improved by making the slit narrower.

As the electron has a wave nature, it will undergo diffraction at the slit giving the pattern as in Figure 2.3. Just at the time of reaching the slit, the velocity v_x of the electron is zero. The formation of the diffraction pattern shows that the electron has developed velocity component v_x after crossing the slit. For the first minimum, the theory of diffraction gives
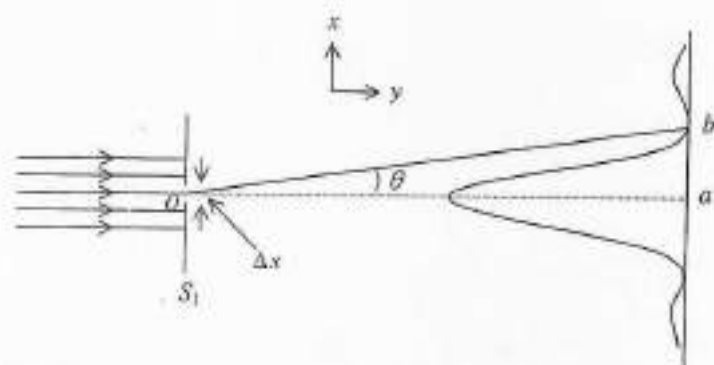
Figure 2.3   Illustration of Heisenberg uncertainty principle—single-slit experiment.

$$\sin \theta \cong \theta = \frac{\lambda}{\Delta x} \tag{2.6}$$

where λ is the wavelength of the electron beam. Let t be the time of transit from o to a and v_{xb} be the value of v_x at b. Then

$$v_0 t = oa \quad \text{and} \quad v_{xb} = \frac{ab}{t}$$

$$\tan \theta \cong \theta = \frac{ab}{oa} = \frac{t v_{xb}}{v_0 t} = \frac{v_{xb}}{v_0} \tag{2.7}$$

From Eqs. (2.6) and (2.7), we get

$$\frac{\lambda}{\Delta x} = \frac{v_{xb}}{v_0}$$

(2.5)

gle-slit experiment

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time of transit

(2.7)

Replacing λ by h/mv_0 and taking v_{xb} as a rough measure of uncertainty Δv_x $= v_x$

$$\frac{h}{mv_0\Delta x} \equiv \frac{\Delta v_x}{v_0} \quad \text{or} \quad \Delta x\Delta p_x \equiv h \tag{2.8}$$

which is the desired relation. In the same way, we have

$$\Delta y\Delta p_y \equiv h \quad \text{and} \quad \Delta z\Delta p_z \equiv h \tag{2.9}$$

As the product of uncertainties is a universal constant, the more precisely we determine one variable, the less accurate is our determination of the other variable.

Before the introduction of the slit, the electrons travelling along the y-axis had the definite value of zero for p_x. By introducing the slit we measured the x-coordinate of the particles to an accuracy Δx, but this measurement introduced an uncertainty into the p_x values of the particles. Thus, the act of measurement introduced an uncontrollable disturbance in the system being measured which is a consequence of the wave particle duality.

Though the result is based on a particular experimental set-up, it is a very general one since it is independent of the particle mass and constants of the apparatus used. Heisenberg assumed it to be a fundamental law of nature. Therefore, the new mechanics we are looking for must abandon the deterministic model and allow only for probable values for dynamical variables.

The new mechanics was formulated independently by Werner Heisenberg (1925) and Erwin Schrödinger (1926). Heisenberg based his mechanics on matrix methods whereas Schrödinger used the idea of wave nature of electron. Introducing relativistic ideas, P.A.M. Dirac generalized quantum mechanics.

Uncertainty Relations for other Variables

Uncertainty relations can also be obtained for other pairs of canonically conjugate variables. For a free particle moving along x-axis, energy E is given by

$$E = \frac{p_x^2}{2m} \quad \text{or} \quad \Delta E = \frac{p_x}{m}\Delta p_x = v_x\,\Delta p_x$$

Therefore,

$$\Delta E = \frac{\Delta x}{\Delta t}\Delta p_x \quad \text{or} \quad \Delta E\,\Delta t = \Delta x\,\Delta p_x$$

Hence

$$\Delta E\,\Delta t \cong h \tag{2.10}$$

This equation indicates that if a system maintains a particular state for time Δt, its energy is uncertain at least by $\Delta E = h/\Delta t$.

The uncertainty for the pair of variables, component of angular momentum along the direction perpendicular to the plane of the orbit (L_c) of a particle and the angular position (ϕ) can be obtained as follows:

$$L_z^2 = 2IE$$

On differentiating, we get

$$L_z \, \Delta L_z = I\Delta E$$

where

$$L_z = I\omega = I\frac{\Delta\phi}{\Delta t}$$

Therefore,

$$I \frac{\Delta\phi}{\Delta t} \Delta L_z = I \Delta E$$

Using Eq. (2.10), we have

$$\Delta\phi \, \Delta L_z = \Delta E \, \Delta t = h \tag{2.11}$$

These uncertainty relations are very useful in explaining number of observed phenomena which the classical physics failed. We shall now consider some of them.

Applications of Uncertainty Relations

Ground state energy of hydrogen atom. The classical expression for the total energy of the electron in the ground state is given by

$$E = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 a} \tag{2.12}$$

where a is the radius of the first orbit. Let the uncertainty in the position of the electron Δx be of the order of a. More correctly, the product of uncertainties is given by h. Therefore,

$$a\Delta p \equiv h \quad \text{or} \quad \Delta p \equiv \frac{\hbar}{a} \tag{2.13}$$

Taking the momentum to be of the order of $\hbar/a$, we get

$$E = \frac{\hbar^2}{2ma^2} - \frac{e^2}{4\pi\varepsilon_0 a} \tag{2.14}$$

For the ground state, the energy E has to be minimum. For this, dE/da must be zero. Denoting the minimum radius by a_0, we have

$$\frac{dE}{da} = 0 = \frac{-\hbar^2}{ma_0^3} + \frac{e^2}{4\pi\varepsilon_0 a_0^2}$$

or

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2} \tag{2.15}$$

With this value of a, Eq. (2.14) becomes

$$E = -\frac{me^4}{(4\pi\varepsilon_0)^2 2\hbar^2} = -\frac{me^4}{8\varepsilon_0^2 h^2} \tag{2.16}$$

which is the ground state energy of the hydrogen atom.

Width of spectral lines.   Spectral lines have finite width due to various factors. One such factor is the natural broadening which is a direct consequence of uncertainty principle. Atoms remain in the excited state for a finite time τ, called the *life time*; before making a transition. Hence there will be an uncertainty in time of the order of τ. Then

$$\tau\Delta E \cong h \quad \text{or} \quad \Delta\nu \cong \frac{1}{2\pi\tau} \tag{2.17}$$

For most of the states, the life time $\tau = 10^{-8}$ s. Hence, $\Delta\nu \cong 10^8$ Hz. This spreading is experimentally observed when the pressure is very low.

Mass of meson.   Yukawa proposed that nuclear forces are due to an exchange of mesons. Uncertainty principle may be used to derive a relation between mass of meson (m) and the range (r_0) of nuclear force. When one nucleon exerts force on the other, a meson is created. During transit, its position is uncertain by an amount r_0. Use of the uncertainty relation gives

$$r_0\Delta p \cong \hbar \quad \text{or} \quad \Delta p \cong \frac{\hbar}{r_0} \tag{2.18}$$

For a relativistic particle $p = mc$. Taking the uncertainty in momentum to be of this order, we obtain

$$mc \cong \frac{\hbar}{r_0} \quad \text{or} \quad m = \frac{\hbar}{r_0 c} \tag{2.19}$$

For $r_0 = 1.5 \times 10^{-13}$ cm, $m \cong 200\, m_e$, where m_e is the electron mass.

Nonexistence of electron in the nucleus.   For an electron to exist inside a nucleus, the uncertainty in its position must be at least of the order of $2r_0$, r_0 being the radius of the nucleus. The uncertainty in the electron momentum is then

$$\Delta p \cong \frac{\hbar}{2r_0} \tag{2.20}$$

For a typical nucleus $r_0 \cong 10^{-14}$ m. Hence

$$\Delta p \cong \frac{1.055 \times 10^{-34}}{2 \times 10^{-14}} \cong 5.28 \times 10^{-21} \text{ kgms}^{-1}$$

The momentum of the electron must at least be of this order. The kinetic energy of the electron

$$T = \frac{p^2}{2m} = \frac{(5.28 \times 10^{-21})^2}{2(9.1 \times 10^{-31})} \, J \equiv 95.7 \, MeV \qquad (2.21)$$

In β-decay, the energy of the emitted electron is usually of the order of few MeV. Therefore one does not expect the electron to be a constituent of the nucleus.

2.3 THE PRINCIPLE OF SUPERPOSITION

Two or more waves can traverse the same space independently of one another. Hence the total displacement at any point due to number of waves is simply the vector sum of the displacements produced by the individual waves. This is known as the *principle of superposition*. This principle is very important in the different branches of physics, namely optics, acoustics, electrical engineering, etc. Superposition principle allows us to analyse a complicated wave motion as a combination of number of simple harmonic motions. Though the linear superposition of waves is important in optics, sound, etc., it is unknown in the classical theory of particles. Since wave motion is assigned to particles in motion, we tentatively extend it to matter waves also. The concept of superposition of states would allow us the construction of wave packets.

2.4 WAVE PACKET

We have already seen that matter exhibits wave-like behaviour under suitable conditions. When the momentum of a particle is well defined, the wave can be of infinite extent. Therefore, a free particle moving along x-axis with a well defined momentum is described by an infinite plane wave $\Psi(x, t)$ given by

$$\Psi(x, t) = A_0 \exp [i(kx - \omega t)] \qquad (2.22)$$

where the wave vector $k = 2\pi/\lambda$ and ω is the angular frequency. In the case of electromagnetic waves, the electromagnetic field varies in space and time. Sound waves can be described by the pressure variation in space and time. In other words, to describe wave motion, one requires a quantity which varies in space and time. In analogy with these, to describe matter waves associated with particles in motion, one requires a quantity which varies in space and time. This variable quantity, called the *wave function*, $\Psi(x, t)$, must be large in regions where the particle is likely to be found and small in the region where it is less likely to be found. That is, the wave function of a particle in conformity with the uncertainty principle must be localized in a small region around it. The wave function of the matter wave which is confined to a small region of space as in Figure 2.4 is termed as a *wave packet* or *wave group*.