

Lecture note- 5

Physical Chemistry CHE 503

QUANTUM CHEMISTRY

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Quantum chemistry – I

4.1 Introduction

Classical mechanics is obeyed by microscopic particles such as planets and rigid bodies. It was formulated by Sir Issac Newton (1642-1727) in the seventeenth century. However microscopic particles such as electrons, protons, atoms molecules show wave duality. They do not obey Newtonian dynamics. They obey quantum mechanics (wave mechanics) a key feature of which is quantization of energy and angular momentum.

From your earlier knowledge, you know that Bhor's theory of hydrogen atom enabled calculation of radii and energies associated with the permissible orbits in the hydrogen atom. The values calculated were found to be in good agreement with experimental values. However, the use of spectroscope of high resolving power reveals the presence of fine structures in the spectra of hydrogen. Bohr's theory could not explain the occurrence of these fine spectral lines.

4.2 Black Body Radiation and Quantum Theory:

Radiation is defined as a wave that consists of oscillating electric and magnetic field; hence, it is also called electromagnetic wave. It is characterised by its wavelength λ and frequency ν (number of oscillations per second) which are related as $\lambda\nu = c$, where c is the velocity of the wave. The value of c is generally $3 \times 10^8 \text{ ms}^{-1}$.

Radiation is emitted by any solid at any temperature as a result of the vibrations of its particles. At low temperature the emitted radiation is of low frequency (large wave length) infrared (human body also gives off infrared radiation but the amount of radiation is very small). As the temperature is raised, not only the amount of radiation increases but also more radiations of smaller frequencies are emitted. At any temperature the radiation from a solid has a continuous range of frequencies (in contrast to gases which produces line spectra).

Different solids emit radiation at different rate at the same temperature, the rate is maximum when the solid is perfectly black (black body). By definition, a black body can absorb all the radiations that falls on it. In practice, a hollow enclosure having a small hole is the nearest approach to a black body because the radiation entering the chamber through the hole is absorbed completely due to repeated reflections inside the enclosure. Radiations emerging from the small hole of such a hollow enclosure is, therefore, called 'black body radiation'. The intensity of radiation, i.e., that total radiation emitted per unit surface area, from a black body depends only on temperature (T) and is independent of the nature of the solid.

4.2.1 Distribution of Energy in the Black Body Radiation:

The radiation emitted by a black body is not confined to a single wavelength but is spread over a wide spectrum of wave lengths. the distribution of radiant energy over the

different frequencies is described in term of a function which denotes the radiant density (amount of radiation per unit volume of the black body chamber) in the frequency range, say ν and $\nu + d\nu$. Experimentally, it is found that any temperature T the energy density increases with wavelength λ^0 , reaches a maximum and then falls of to zero. As temperature increases the point of maximum shifts to higher frequency (shorter wavelength) side. The experimental dependence of the energy density on temperature and wave length (λ) is shown in Fig.4.1

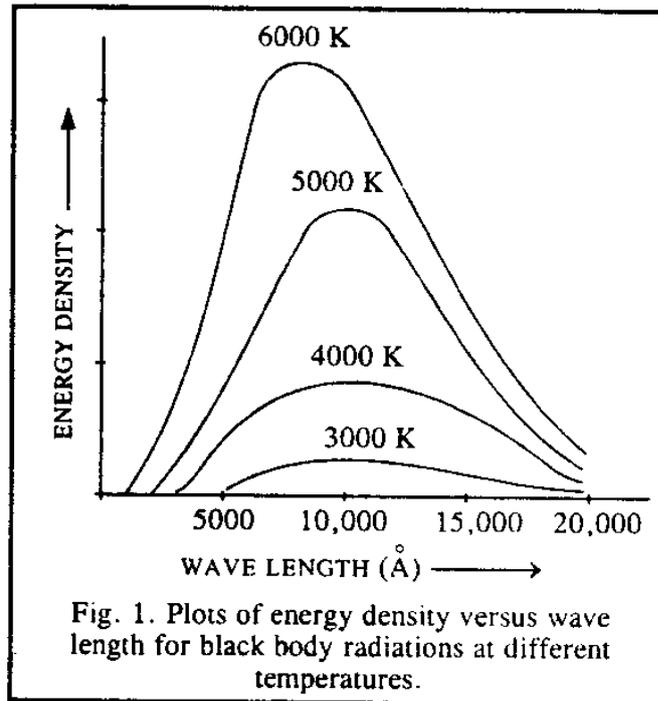


Fig 4.1 Dependence of energy density on wavelength and temperature

The curves so obtained have the following characteristics.

The radiation emitted by a black body is not confined to a single wavelength but spread over a wide spectrum of wavelengths. The distribution of radiant energy over the different frequencies is described in terms of a function $\rho(\nu)d\nu$ which denotes the radiant energy density (amount of radiation per unit volume of the black body chamber) in the frequency range ν and $\nu + d\nu$.

- (i) For each temperature, there is a particular wavelength at which the energy radiated is maximum.
- (ii) The position of maximum shift toward lower wavelength with increase in temperature.
- (iii) The higher the temperature, the more pronounced is the maximum.

These curves are usually referred to the black body radiation curves. A perfect absorber is also a perfect emitter of radiation. Thus of all bodies heated to a given temperature, maximum energy is radiated by black body.

According to Wien's displacement law, $\lambda_m T = b$, where λ_m is the wavelength corresponding to maximum in the curve the wein constant $b = 0.0029 \text{ mK}$. wein, the german physicist, was awarded the 1911 Physics Nobel prize for his discovery concerning the laws governing the heat radiation.

4.3 Quantum Theory of Radiation:

The energy distribution in black body radiation is could not be explained by the application of classical physics. The correct expression was derived by Plank on the basis of quantum theory of radiation. According to this theory,

- (1) Radiant energy is emitted or absorbed discontinuously in the form of tiny bundles of energy known as quanta.
- (2) Each quantum is associated with definite amount of energy $E(= h\nu)$ where E is energy in Joules, ν is frequency of radiation in reciprocal of second(s^{-1}) and h is fundamental constant known as Plank's constant. The numerical value of h is 6.626×10^{-24} Js.

The value of quantum energy is given by $hc\bar{\nu}$ where $\bar{\nu}$ is the wave number defined as reciprocal of wavelength i.e., $\bar{\nu} = \frac{1}{\lambda}$. evidently, $\nu = \frac{c}{\lambda} = c\bar{\nu}$ and $E = hc\bar{\nu}$.

- (3) A body can emit or absorb energy only in whole number of quantum. i.e., $1h\nu, 2h\nu, 3h\nu, \dots, nh\nu$. Energy in fractions of quantum cannot be lost or absorbed. This is known as quantization of energy.

Based on this theory, Plank obtained the following expression for the energy density of black body radiation.

$$E(\nu)d\nu = \frac{8\pi h\nu^3}{c^3} \times \frac{d\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \dots\dots\dots(4.1)$$

4.4 Photoelectric Effect:-

J.J. Thomson observed that when a beam of light of sufficiently high frequency is allowed to strike a metal surface in vacuum, electron are ejected from the metal surface. This phenomenon is known as photoelectric effect and the ejected electron photoelectrons

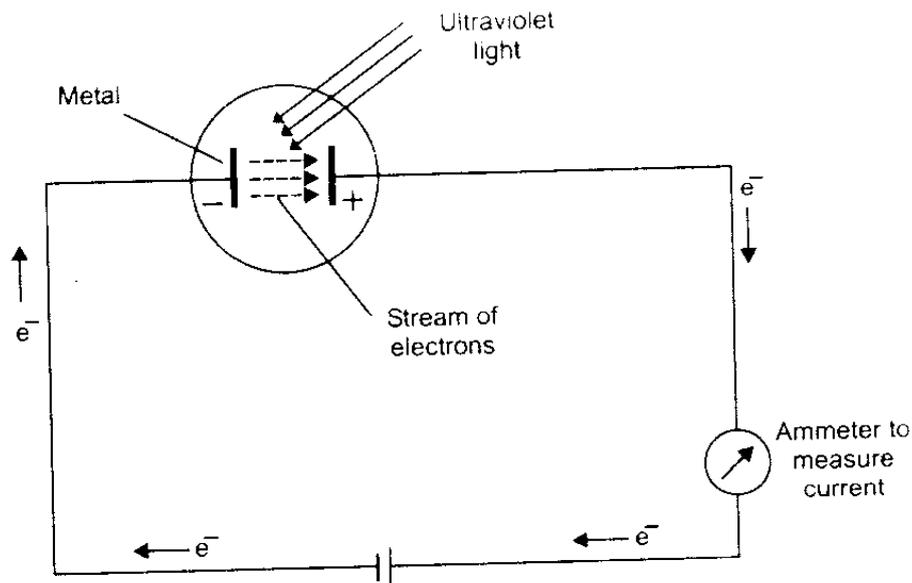


Fig.4.2 Photoelectric effect

A few metals show this effect under the action of visible light, but many more show under the action of more energetic ultraviolet light. Cesium, which amongst the alkali metals has the lowest ionization energy, is also the metal from which electrons are ejected most easily by light. This metal is, therefore, used largely in photoelectric cells.

After making careful study of photoelectric effect under different conditions, the following observations were made:

- (1) For each metal, a certain minimum frequency of incident light is needed to eject electrons. This is known as threshold frequency, ν_0 . A light of lower frequency than this cannot eject electrons no matter how long it falls on metal surface or how long is its intensity. The threshold frequency is different for different metals.
- (2) The kinetic energy of ejected electrons is independent of the intensity of incident light but varies linearly with its frequency.
- (3) The number of ejected electrons from the metal surface depends upon the intensity of the incident radiation. The greater the intensity, the larger is the number of ejected electrons.

4.4.1 Einstein's Photoelectric Equation:

The Photoelectric effect cannot be explained on the basis of the classical wave theory of light. According to this theory, energy of light depends on its intensity. If this view is correct, then the light of any frequency, if made sufficiently intense, can cause ejection of electrons. But this does not happen. The quantum theory of radiation affords an easy explanation for the photoelectric effect. According to this theory, light consists of bundles of energy called photons. The energy of each photon being equal to $h\nu$ where ν is the frequency of light. When a photon of light of frequency ν_0 (threshold frequency) strikes on an electron in a metal, it imparts its entire energy ($= h\nu_0$) to the electron. This energy enables the electron to break away from the atom by overcoming the attractive influence of the nucleus. Thus each photon can eject one electron. If the frequency of light is less than ν_0 ,

there will be no ejection of electron. Now suppose frequency of the light falling on the metal surface is higher than the threshold frequency. Let it be ν . When the photon of this light strikes a metal surface, some of its energy (which is equal to the energy binding the electron with the nucleus) is consumed to separate the electron from the metal and the remaining energy will be imparted to the ejected electron to give it certain velocity u (i.e., kinetic energy $\frac{1}{2}mu^2$). Einstein, applying quantum theory, showed that

$$h\nu = \phi + \frac{1}{2}mu^2 \quad \dots\dots\dots(4.2)$$

Where ϕ is threshold energy (or the work function) of the metal and $\frac{1}{2}mu^2$ is the kinetic energy imparted to the ejected electron. Evidently,

$$\phi = h\nu_0 \quad \dots\dots\dots(4.3)$$

Substituting the above value of ϕ in the equation (4.2) and rearranging, we get

$$\frac{1}{2}mu^2 = h(\nu - \nu_0) \quad \dots\dots\dots(4.4)$$

Equation 4.4 is the Einstein photo electric equation. Albert Einstein (1879- 1955), the German physicist, won the noble prize in 1921 for explaining the photoelectric effect and other contribution to mathematical physics.

4.5 Compton Effect

In 1923 Compton provided one more proof of quantum theory. The American physicist shared in 1927 Physics novel prize With Wilson, The British physicist Arthur Compton found that if monochromatic X-rays (i.e., X rays having a particular wavelength) are allowed to fall on carbon or some other light element, the scattered X rays have wavelength lighter than the incident rays. In other words, the scattered X rays have lower frequency, i.e., lower energy than the incident X rays. Since the scattering is caused by electrons, it is evident that some interaction between X rays and electrons have taken place and this is resulted in decrease in energy for the former. The decrease in energy or increase in wavelength of X rays after scattering from the surface of an object is known as **Compton Effect**.

Compton demonstrated that:

When X rays of wavelength λ' struck a sample of graphite, an electron was ejected and the X- ray scattered at an angle θ had longer wavelength λ .

By applying the law of conservation of energy and law of conservation of momentum and assuming X-ray to consist of photons, each possessing energy $h\nu$, Compton showed that

$$\Delta \lambda = \left(\frac{2h}{mc}\right) \sin^2 \frac{\theta}{2} \quad \dots\dots\dots(4.5)$$

Where $\Delta \lambda = (\lambda - \lambda')$ is the increase in wavelength (termed as Compton shift) produced as a result of the collision, m is the rest mass of the electron, c is the velocity of light and θ is the angle between the incident and the scattered X-ray.

According to this equation, Compton shift should be independent of the wavelength of the incident X-ray. This has been found to be so experimentally. Further, the value of Compton

shift, as obtained from the above equation, by substituting the values of λ, c, m and θ have been found to be in close agreement with the experimental values.

Compton said that it was like a ball hitting a stationary ball which is pushed away while the energy of the striking ball decreased. Compton effect provides a good illustration of the uncertainty principle. Suppose X-rays are used to determine the position and momentum of an electron. As a result of mutual interaction of X-rays and electron the wavelength of X-rays increases, i.e., the frequency or energy of X-ray decreases. This energy must have been transferred to the electron and, therefore, the momentum of the electron must have changed during the process. Consequently, the momentum of the electron cannot be determined with certainty.

Compton effect also provides for the photon nature of radiation. The Compton equation (a) can be written as

$$\Delta \lambda = \lambda - \lambda' = \frac{h}{mc} (1 - \cos \theta) \quad \dots\dots\dots(4.6)$$

We see that the wavelength λ' of scattered X-rays is always greater than the wavelength λ of the incident X-rays. The wavelength shift is independent of the nature of the substance and the wavelength of incident X-ray. It depends on the scattering angle θ only.

4.6 The Sommerfeld Extension of Bohr's Theory:

Bohr could not explain the presence of fine structure. The theory was extended by German mathematical physicist Arnold Sommerfeld (1868 – 1951), by putting forward the idea of elliptical orbits.

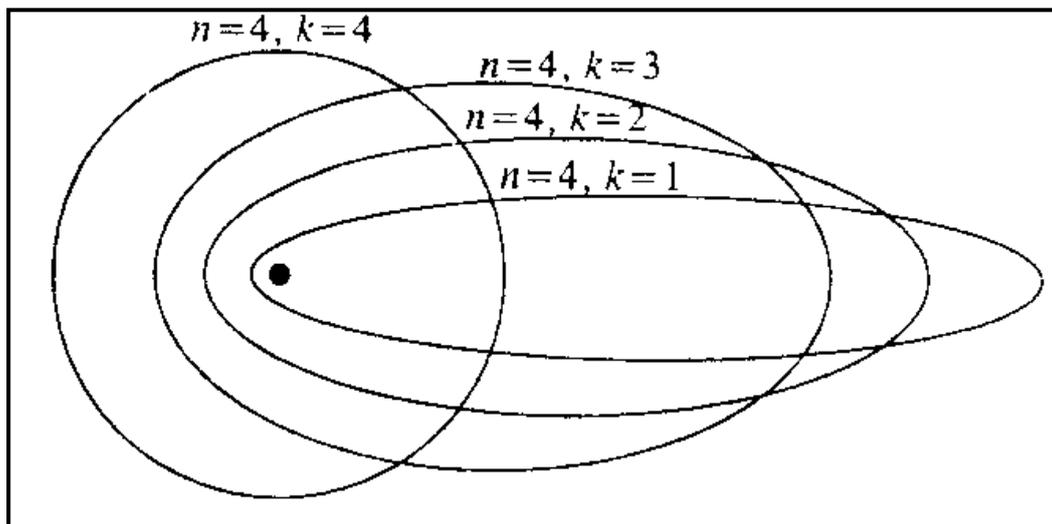


Fig. 4.3 Sommerfeld's elliptical electron orbit for n=4

According to Sommerfeld, an electron revolving around a central positively charged nucleus is so influenced by the nucleus charge that it is set into elliptical orbits with the nucleus situated at one of the foci (Fig.4.3). That is clear that while according to Bohr's theory electron move in circular orbits, according to Sommerfeld's modification, electron move in elliptical orbits. In Sommerfeld modification, there will be a major axis and a minor axis having

different lengths. As the orbit broadens, the lengths of two axes become closer and they become circular as shown in Fig.4.3. Thus, the circular orbit is special case of elliptical orbit.

4.7 Weakness of Bohr's Theory:

The Bohr's theory of the atom gave a surprisingly accurate quantitative explanation of the spectra of atom and ions with a single electron. However, with atom of two electrons [He], serious discrepancies with experiment were encountered. The main shortcomings of Bohr's theory are as follows:

1. Bohr's theory fails to explain spectra of multi electron atoms.
2. Bohr's atomic model fails to account for the effect of magnetic field on the spectra of atoms and ions. It is observed that when the source of spectrum is placed in a strong magnetic field, each spectral line is further split into numbers of lines, this is called Zeeman effect. This observation cannot be explained on the basis of Bohr's model.
3. In 1923, de Broglie suggested that electron like light has a dual character. It has particle as well as wave character. Bohr's theory treats the electron as a particle.
4. According to Heisenberg's uncertainty principle, it is impossible to determine simultaneously the exact position and momentum of a small moving particle like electron. The postulate of Bohr that the electrons revolve in well defined orbit around the nucleus with well defined velocities is, not tenable. Now we shall discuss de Broglie's concept and Heisenberg's uncertainty principle in some details since these two concepts are mainly responsible for exposing the most serious shortcomings off Bohr's theory.

4.8 Wave Theory of Matter

4.8.1 Particle and Wave Character of Electron:

de Broglie's Equation: In 1905 Einstein had suggested that light has a dual character ; as 'wave' and also as 'particle'. De Broglie in 1924 suggested that any moving material particle has associated wave properties. de Broglie deduced that the laws of optics differ from the laws of ordinary mechanics only because of the rest mass of photons is zero. Hence de Broglie reasoned particles with small masses such as electrons, protons, neutrons, atoms, molecules etc. shows dual character. de Broglie was awarded the Physics Noble prize in 1929.

Example:

Calculate the de Broglie wavelength of electron moving with the velocity 1.2×10^5 m/sec.

Solution:

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

$$= \frac{6.626 \times 10^{-34} \text{Js}}{(9.1 \times 10^{-31} \text{Kg})(1.2 \times 10^5 \text{ms}^{-1})}$$

$$= 6.068 \times 10^{-9} m$$

$$= 6.068 \text{Å}$$

4.8.2 Heisenberg Uncertainty Principle:

Werner Heisenberg, In 1927 enunciated one of the most fundamental relationship of modern physics which is known as uncertainty principle. According this principle 'it is impossible to make simultaneously, the exact determination of the velocity of a particle and also its position.' In the word of British cosmologist Stephan Hawking , 'even god is bound by the uncertainty principle and cannot predict future exactly'. The uncertainties in the determination of these two quantities vary inversely so that, if one is determined fairly accurately, the other must be correspondingly less accurate, this limitation is in no way dependent upon the accuracy of the observing instruments or the method of the measurements, but it an inherent relationship in nature applicable to all particles.

If p and x represents two conjugate variables, such as momentum and position of any particle, the product of the uncertainties Δp and Δx in the determination of their respective values is approximately given by the following relation,

$$(\Delta x)/(\Delta p) \geq h/4\pi \quad \dots\dots\dots(4.7)$$

Where Δx is uncertainty with regard to its position and Δp is the corresponding uncertainty with regard to its momentum. Evidently if (Δx) is very small, i.e. The position of the particle is known more or less exactly, Δp would be large, i.e., uncertainty with regard to momentum will be large. Similarly, if an attempt is made to measure exactly the momentum of the particle, the uncertainty with regard to position will become large. The German physicist, Werner Heisenberg (1900-1976) won the physics Noble prize in 1932.

If we measure the position to within 1.0 nm, about the resolving power of an electron microscope, $\Delta y = 10^{-7}$ and hence $\Delta v = 10^{-7} \text{ cms}^{-1}$, with this indeterminacy in velocity, the position one second later would be uncertain to within 2.0 nm. or about 0.2% of the diameter of the particle. Thus, even in the case of ordinary microscopic particle, indeterminacy may limit exact measurements. With particle of atomic or subatomic size, the effect will be much greater.

When waves are associated with particles, an uncertainty principle is a necessary consequence. If the wavelength or frequency of an electron wave is to have a definitely fixed value, the wave must have an infinite event. Any attempt to confine a wave within boundaries requires destructive interference at the boundaries to reduce the amplitudes there to zero. It follows that an electron wave of perfectly fixed frequency, or momentum, must be infinitely extended and therefore must have a completely intermediate position. To fix the position, we require superimposed waves of different frequency and thus as the position becomes more closely defined, the frequency and hence momentum becomes less precisely specified.

The uncertainty principle relation can also be expressed in terms of energy and time. Thus,

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{4\pi} \dots\dots\dots(4.8).$$

To measure the energy of system with an accuracy ΔE , the measurement must be extended over a period of time of order of magnitude $\frac{\hbar}{\Delta E}$. This equation is used to estimate the sharpness of spectral lines. In general, lines arising from transition from the ground state of an atom are sharp, because the optical electron spend a long time Δt in the ground state and ΔE the uncertainty in the energy level, is correspondingly small, the line breath is related to ΔE by $\Delta \nu = \frac{\Delta E}{h}$. The life time of excited states may sometimes be very short and transition between such states give rise to diffuse lines as a result of the indeterminacy of the energy levels.

4.8.3 Physical Concept of Uncertainty Principle:

The physical concept of uncertainty principle becomes illustrated by considering an attempt to measure the position and momentum of an electron moving in Bohr's orbit. To locate the position of the electron, we shall devise an instrument 'super microscope' to see the electron. A substance is said to be seen only if it could reflect light or any other radiation from its surface. Because the size of electron is very small, its position in any instant may be determined by a super microscope employing light of very small wave length (such as x-rays or γ rays).

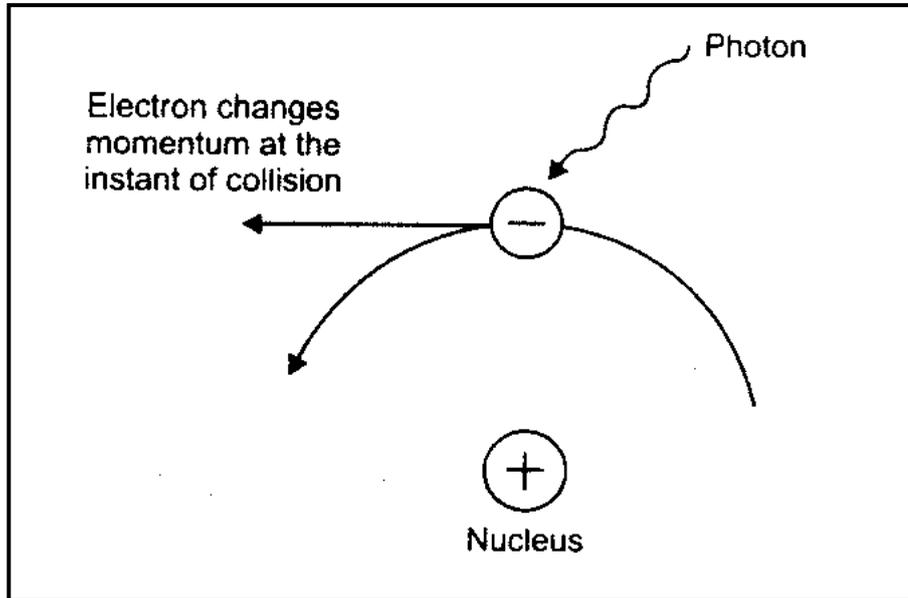


Fig 4.4 The momentum of electron changes when the photon of light strikes it, so does its position

A photon of such a radiation of small wave length λ , has great energy and therefore has large momentum. As one such photon strikes the electron and is reflected, its intensity changes the momentum of electron. Now the momentum gets changed and becomes more uncertain as the position of the electron is determined (Fig 4.4). Thus it is impossible to

determine the exact position of an electron moving with a definite velocity (or possessing definite energy). It appears clear that Bohr's picture of as electrons moving in a orbit with fixed velocity (or energy) is completely untenable.

As it is impossible to know the position and velocity of any one electron on account of its small size, the best we can do is to speak of the probability or relative change of finding an electron with a probable velocity. The old classical concept of Bohr has now been discarded in favour of the probability approach.

Before we take on the detailed study of quantum mechanics let us study first that what are conservation laws and classical mechanics.

4.9 Conservation Laws and Classical Mechanics.

4.9.1 Newtonian Mechanics:

For our purposes Newtonian mechanics consist of the verbal and mathematical statements of Newton's three laws of motion, which, together with a few definitions, allow us to derive the conservation laws.

4.9.2 First Law (Law of Inertia). Everybody tends to remain at rest or in uniform motion (constant velocity) in a straight line unless acted upon by a external force.

4.9.3 Second Law (Law of Force). The rate of change of momentum is proportional to the force producing it.

4.9.4 Third Law (Law of Action and Reaction). If body A exert a force on a body B this is equivalent to body B exerting a force equal magnitude but opposite in sign on body A. the mathematical statement of the second law is:

$$F = \frac{dp}{dt} \dots\dots\dots(4.9)$$

This leads directly to the important results of Newtonian mechanics. F is total force acting on the body and p is momentum of the body defined as

$$p = mv = m \frac{dr}{dt} \dots\dots\dots(4.10)$$

where m is the mass of the particle and v is the velocity and r is the radial vector from the origin to the position of the body.

4.10 Distinction Between Matter Waves and Electromagnetic Waves:

It should be carefully noted that matter waves are distinctly different from electromagnetic waves. The speed of these waves is not the same as that of light; it is understandably, much less. These waves cannot be radiated in empty space. They are not emitted by the particle under consideration; they are simply associated with it. The wavelength of matter waves are generally very small as compared to wavelength of electromagnetic waves.

4.11 Derivation of Bohr Angular Momentum Postulate from de Broglie's Relation

Consider an electron moving in a circular orbit of radius r around a nucleus. The wave train would be as shown in Fig. (4.5). Evidently, if the wave is to remain continually in phase Fig. (4.5a), the circumference of the circular orbit must be an integral multiple of wavelength λ , that is

$$2\pi r = n\lambda = \frac{nh}{mv} \quad \dots\dots\dots(4.11)$$

Thus, angular momentum, $L = mvr = \frac{n\lambda}{2\pi} \quad \dots\dots\dots(4.12)$

This is Bohr's postulate.

Evidently, if the circumference is bigger or smaller than the value $\frac{nh}{2\pi}$, the wave will not longer remain in phase

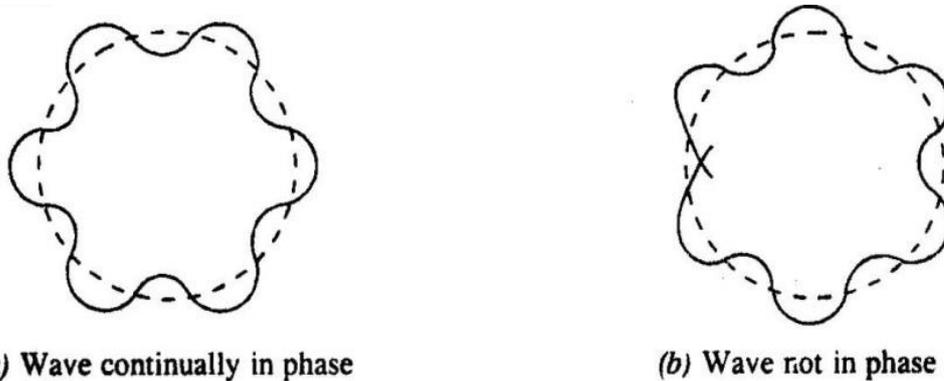


Fig. 4.5 The wave trains of an electron moving in a circular path around a nucleus

4.12 Quantum Mechanics:

The microscopic particles such as protons, electrons, atoms and molecules show wave particle duality. They do not obey Newtonian dynamics. The laws of quantum mechanics (or wave mechanics) were formulated in 1925 by the German physicist. M. Born ,W. Heisenberg and P. Jordon (in the formulation known as metrix mechanics) and in 1926 by Austrian physicist E. Schrodinger. Schrodinger formulation of quantum mechanics is more familiar to chemists than the Born Heisenberg–Jordon formulation of metrix mechanics through both are equivalent.

4.12.1 The Postulates of Quantum Mechanics :

The postulates of quantum mechanics for the mechanical treatment of the structure of atom rest upon a few postulates which, for a system moving in one dimension, say the x -coordinate, are given below.

First postulate: The physical state of a system at time t is described by the wave function $\psi(x,t)$.

S

Second postulate: The wave function ψ and its first and second derivative $\psi(x,t)/\delta x$ and $\delta^2\psi(x,t)/\delta x^2$ are continuous, finite and single valued for all values of x . And also the wave function $\psi(x,t)$ is normalized, i.e.,

$$\int_{-\infty}^{+\infty} \psi^*(x,t)\psi(x,t) dx = 1 \quad \dots\dots\dots(4.13)$$

Where ψ^* is complete conjugate of ψ formed by replacing i with $-i$ wherever it occurs in the function $\psi(i=\sqrt{-1})$.

Third Postulate: A physically observable quantity can be represented by a Hermitian operator. An operator is said to be Hermitian operator, \hat{A} if it satisfies the following condition:

$$\int \psi_i^* \hat{A} \psi_j dx = \int \psi_j (\hat{A} \psi_i^*) dx \quad \dots\dots\dots(4.14)$$

Where ψ_i, ψ_j are the wave functions representing the physical states of the quantum system, i.e., a particle, an atom or molecule.

Fourth postulate: The allowed value of an observable A are the eigen-values, a_i in an operator equation

$$\hat{A} \psi_i = a_i \psi_i \quad \dots\dots\dots(4.15)$$

Eq. (4.15) is known as an eigen-value equation. Here \hat{A} is the operator for the observable (physical quantity) and ψ_i is an eigen value a_i . In other words, the measurement of the observable A yield the eigen value a_i .

Fifth postulate: The average value (or expectation value), $\langle A \rangle$ of an observable A corresponding to the operator \hat{A} is obtained from the relation

$$\langle A \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{A} \psi dx \quad \dots\dots\dots(4.16)$$

Where the function ψ is assumed to be normalized in accordance with Eq.4.13. The average value of, say, the x - coordinate is given by

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{x} \psi dx \quad \dots\dots\dots(4.17)$$

Sixth postulate: The quantum mechanical operators corresponding to the observable are constructed by writing the classical expression in terms of the variables and covering the expressions to the operators, as shown in table

TABLE 1
Wave Mechanical Operators for Evaluating Various Classical Variables

Classical variable	Quantum mechanical operator	Operator	Operation
x	\hat{x}	x	Multiplication by x
p_x	\hat{p}_x	$-i\hbar \frac{\partial}{\partial x}$	Taking derivative with respect to x and multiplying by $-i\hbar$
x^2	\hat{x}^2	x^2	Multiplication by x^2
p_x^2	\hat{p}_x^2	$-\hbar^2 \frac{\partial^2}{\partial x^2}$	Taking second derivative with respect to x and multiplying by $-\hbar^2$
t	\hat{t}		Multiplying by t
E	\hat{E}	$i\hbar \frac{\partial}{\partial t}$	Taking derivative with respect to t and multiplying by $i\hbar$

Seventh postulate: The wave function $\psi(x,t)$ is a solution of the time-dependent equation $\hat{H} \psi(x,t) = i\hbar \frac{\partial \psi(x,t)}{\partial t}$ (4.18)

Where \hat{H} is the Hamiltonian operator of the system.

4.12.2 Zero point energy: According to old quantum theory, the energy levels of harmonic oscillators were given by $E_v = nh\nu$. If there were true the lowest energy level, with $v = 0$, would have zero energy. This would be a state of complete rest, represented by the minimum in the Fig. 4.6.

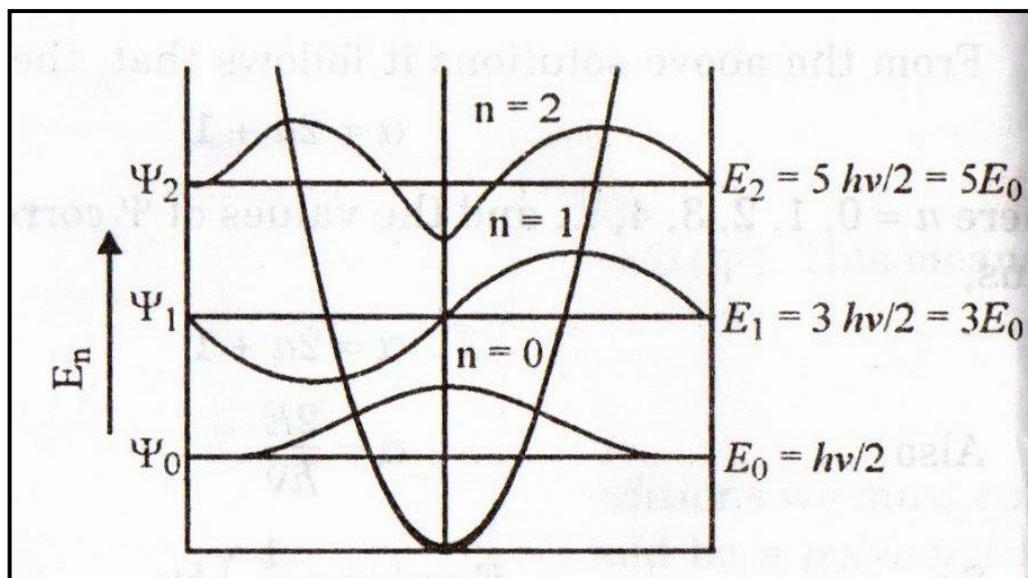


Fig.4.6 Various energy levels.

The uncertainty principle does not allow such a state of completely defined (in case of zero) momentum. Consequently, the wave treatment shows that the energy levels of the oscillators are given by

$$E_v = (v + \frac{1}{2}) h\nu \quad \dots\dots\dots(4.19)$$

Now when $v = 0$, the ground state, there is residual zero point energy amounting to

$$E_0 = \frac{1}{2} h\nu \quad \dots\dots\dots(4.20)$$

4.13 The Schrödinger Wave Equation.

4.13.1 Derivation of The Schrödinger Wave Equation

Ervin Schrödinger and Werner Heisenberg independently discovered the basic principles for a new kind of mechanics, which provided mathematical techniques competent to deal with the wave particle duality of matter and energy. The formalism of Schrödinger was called wave mechanics and that of Heisenberg matrix mechanics. Despite their quite different mathematical formalism, the two methods of essentially equivalent at the deeper level of their physical concepts. They represent two different forms of fundamental theory called quantum mechanics.

In the derivation of wave equation, Schrödinger made use of the de Broglie relationship between the momentum of a particle and the wavelength of the associated matter waves. This represents the essential postulatory basis of Schrödinger approach to the new mechanics. In Schrödinger wave model of an atom, the discrete energy levels or orbits proposed by Bohr are replaced by mathematical functions, ψ , which are related to the probability of finding electrons at various places around nucleus.

Consider a simple wave motion as that of the vibration of a stretched string. Let ω be the amplitude of this vibration of any point whose coordinate be x at time t . the equation of such a wave motion may be expressed as:

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{1}{u^2} \times \frac{\partial^2 \omega}{\partial t^2} \quad \dots\dots\dots(4.21)$$

Where u is the velocity with which the wave is propagating. There are two variables, x and t , in the above differential equation, i.e., the amplitude ω depends upon two variables x and t . This differential equation may be solved by separating the variables, thus ω may be expressed in the form

$$\omega = f(x)g(t) \quad \dots\dots\dots(4.22)$$

Where $f(x)$ is a function of coordinate x only and $g(t)$ is a function of time t only. For stationary waves, such as which occurs in the stretched string, the function $g(t)$ be represented by the expression

$$g(t) = A \sin(2\pi vt) \dots\dots\dots(4.23)$$

where v is the vibrational frequency and A is a constant known as the maximum amplitude.

Hence The equation for ω may then be written as,

$$\omega = f(x)A \sin(2\pi vt) \dots\dots\dots(4.24)$$

Differentiating equation (4.24) with respect to t ,

$$\frac{\partial \omega}{\partial t} = f(x)A \cos(2\pi vt).2\pi v$$

$$\text{And } \frac{\partial}{\partial t} \left(\frac{\partial \omega}{\partial t} \right) = -f(x)A \sin(2\pi vt).4\pi^2 v^2 \dots\dots\dots(4.25)$$

$$\text{or } \frac{\partial^2 \omega}{\partial t^2} = -4\pi^2 v^2 f(x)g(t) \dots\dots\dots(4.26)$$

Similarly from equation (4.22)

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{\partial^2 f(x)}{\partial x^2} g(t) \dots\dots\dots (4.27)$$

From equations (4.21),(4.26) and (4.27), we

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{-4\pi^2 v^2}{u^2} f(x) \dots\dots\dots(4.28)$$

The frequency of the vibrations, v and the velocity, u are related by the expression

$u = \lambda v$, where λ is the corresponding wavelength. Hence from equation (4.28), we get

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2}{\lambda^2} f(x) \dots\dots\dots(4.29)$$

Now schrödinger wave may be formulated by combining two relationships. one is based on purely mathematical property of waves, namely equation (4.29) and the other is on the wave property of matter as represented by Broglie equation, (i.e., $\lambda=h/mu$).

The equation (4.29) represents wave motion in one direction only. It may be extended to movement in three directions represented by the coordinate x, y and z . if $f(x)$ for one coordinate is represented by $\psi(x, y, z)$ which is amplitude function for three coordinate, equation (4.29). Takes the form,

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} = \frac{-4\pi^2}{\lambda^2} \varphi \dots\dots\dots(4.30)$$

Here φ is a function of Cartesian coordinates (x, y, z) . Replacing the symbol ∇^2 (pronounced as del square) for the differential (Laplacian) operator, i.e

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

We get
$$\nabla^2 \varphi = \frac{-4\pi^2}{\lambda^2} \varphi \quad \dots\dots\dots(4.31)$$

Following the de Broglie ideas, Schrödinger, the Austrian physicist, applied the above treatment to material waves associated with all particles including electrons, atoms and molecules. Upon introducing de Broglie relationship, $\lambda = h/mu$ in equation (4.31)

$$\nabla^2 \varphi = \frac{-4\pi^2 m^2 u^2}{\lambda^2} \psi \quad \dots\dots\dots(4.32)$$

Where m is the mass and u is the velocity of the particle.

The kinetic energy of the particle given by $\frac{1}{2}mu^2$, is equal to the total energy E minus the potential energy (V) of the particle, i.e.,

$$\begin{aligned} \text{K.E.} &= \frac{1}{2}mu^2 = E - V \\ \text{or } mu^2 &= 2(E - V) \quad \dots\dots\dots(4.33) \end{aligned}$$

Combining equation (4.32) and equation (4.33) we get

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} + \frac{8\pi^2 m(E - V)}{\lambda^2} \varphi = 0 \quad \dots\dots\dots(4.34)$$

or
$$\nabla^2 \varphi + \frac{8\pi^2 m(E - V)}{\lambda^2} \varphi = 0 \quad \dots\dots\dots(4.35)$$

These two equations (4.34) and (4.35) are the wave equations for a simple particle. Either of these equations are called as Schrödinger wave equation which has been used to solve a number of problems related to the atomic and molecular structure.

Schrödinger shared the 1933 physics noble prize with Dirac for the discovery of new productive forms of atomic theory.

The Schrodinger's Wave equation is a second degree differential equation. It has several solutions. Some of these are imaginary and not valid. If the potential energy is known, the total energy E and corresponding wave function φ can be evaluated.

The wave function is always finite, single valued and continuous. It is zero at infinite distance. Solutions that meet these requirements are only possible, if E is given certain characteristic values called **eigen-values**. Corresponding to these values of E , we have certain characteristic values of wave function φ and are called **eigen-functions**. As these eigen-values correspond very nearly to the energy values associated with different Bohr-orbits, the Bohr model may be considered as a direct consequence of wave mechanical approach.

4.14 Significance of ψ and ψ^2

In the Schrödinger wave equation we have used the function ψ as a quantity analogous to amplitude in classical wave. According to the theory of propagation of light and sound waves, the square of the amplitude of the wave is proportional to the intensity of sound or light. A similar concept, modified to meet the requirement of uncertainty principle, has been developed for the physical interpretation of wave function ψ .

A physical interpretation is given to ψ^2 rather than ψ itself. For an electromagnetic wave, Einstein interpreted ψ^2 at a point as ‘probability density’, i.e., probability per unit space of finding the proton at that point. A simple interpretation was given by the Max Born to ψ^2 for a particle wave. If a particle is moving in one dimension, ψ^2 or $\psi^*\psi$ represents probability of findings it within unit distance. Then in infinitesimal dx around a point, the probability is $\psi^2 dx$ or $\psi^*\psi dx$, ψ being a function of x only. In three dimensions space, the probability is $\psi^2 dx dy dz$ or $\psi^*\psi dx dy dz$ where $\psi = \psi(x, y, z)$ and it refers to the probability that the x , y and z coordinate of the particle lie within $x + dx$, $y + dy$ and $z + dz$ respectively. For a system of n particles in three dimensions, each will have its own set of coordinates the probability can be extended accordingly.

For an electron wave, an alternative and more useful interpretation of ψ^2 or $\psi^*\psi$ is given in terms of “electron density, i.e., electronic charge per unit space”. This arises from the concept that the electron being a wave may be supposed to behave like a cloud of negative electricity with non-uniform charge distribution.

The Schrodinger’s wave equation is a second degree differential equation. It has several solutions. Some of these are imaginary and are not valid. If the potential energy term is known, the total energy E and corresponding wave function ψ can be evaluated.

The wave function is always finite, single valued and continuous. It is zero at infinite distance. Solutions that meet these requirements are only possible, if E is given certain characteristic values called **eigen-values**. Corresponding to these values of E , we have certain characteristic values of wave function ψ and are called **eigen- function**. As the eigen-values correspond very nearly to the energy values associated with different Bohr-orbits, the Bohr model may be considered as a direct consequence of wave mechanical approach.

4.15 Conclusion:

In classical mechanics, the state of a system is defined by specifying all the forces acting and all the positions and velocities of the particles. Thus a knowledge of the present state of a classical mechanical system allows its future state to be predicted with certainty. In quantum mechanism, as you have studied till now, the state of a system is defined by the wave function ψ which is a function of the coordinates of the particles of the system and a function of time. The time-dependent Schrodinger Wave Equation is the quantum mechanical analogue of Newton’s Second Law which allows the future state of a quantum mechanical system to be predicted from its present state. It should be clear to you that the knowledge of the state in quantum mechanism usually involves knowledge of only probabilities rather than certainties.

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