Chapter 1

Basic Principle of Quantum Chemistry

Introduction (Philosophical View)

Unlike ***Newton's*** mechanics, or ***Maxwell's*** electrodynamics, or ***Einstein's*** relativity, quantum theory was not created or even definitively packaged and it retains to this day some of the scars of its exhilaranting but traumatic youth. There is no general consensus as to what its fundamental principles are, how it should be taught, or what it really "means". ***Niels Bohr*** said, "If you are not confused by quantum physics then you haven't really understood it", ***Richard Feynman*** remarked, "I think I can safely say that nobody understands quantum mechanics."

Teaching quantum mechanics without the appropriate mathematical equipment is like asking the student to dig a foundation with a screwdriver.

The first step in the development of a logically consistent theory of non-relativistic quantum mechanics is to devise a wave equation which can describe the covert, wave-like behaviour of a quantum particle. This equation is called the ***Schrodinger*** equation. The role of the Schrodinger equation in quantum mechanics is analogous to that of Newton's Laws in classical mechanics. Both describe motion. Newton's Second Law is a differential equation which describes how a classical particle moves, whereas the Schrodinger equation is a partial differential equation which describes how the wave function representing a quantum particle ebbs and flows. In addition, both were postulated and then tested by experiment.

In classical physics, fundamental laws of physics are used to derive the wave equations which describe wave-like phenomena; for example, Maxwell's laws of electromagnetism can be used to derive the classical wave equation which governs electromagnetic waves in the vacuum. In contrast, we shall view the equation governing the wave-like properties of a quantum particle as a fundamental equation which cannot be derived from underlying basic physical principles. We, like the inventors of quantum theory, can only guess the form of this wave equation and then test for consistency and agreement with experiment.

According to de-Broglie:

It was possible to associate waves with every moving particles in nature. This relation should hold also for heavier particles which we are able to see. But, on account of heavier mass, λ becomes so small that there is a great difficulty in discovering the wave phenomenon associated with heavier particles. This concept of the wave-particle duality of matter was subjected to experiment test by ***Davisson*** and ***Germer*** in 1927 and independently by ***Thompson*** in 1928 who showed that a beam of electrons did indeed behave as if it were waves and underwent diffraction from a suitable grating.

If electrons have the wave properties then there must be a wave equation and a wave function to describe the electron waves just as the waves of light, sound and strings are described.

New Discoveries Prompted the Need for a better theory to describe the behaviour of matter at the atomic level. This better theory, called quantum mechanics, represented a completely new way of modeling nature. Quantum mechanics ultimately showed that it provides a better basis for describing, explaining, and predicting, behaviour at the atomic and molecular level. As with any theory in science, quantum mechanics is accepted by scientists because it works. (It is, quite frankly, one of the most successfully tested theories devised by science.) That is, it provides a theoretical background that makes predictions that agree with experiment. **There may be certain conceptual difficulties at**

first. A common question from a student is "Why is quantum mechanics this way?" The philosophy of quantum mechanics is left to the philosopher. Here, we want to see how quantum mechanics is defined and how to apply it to atomic and molecular systems.

Quantum mechanics is based on several statements called postulates. These postulates are assumed, not proven. It may seem difficult to understand why an entire model of electrons, atoms, and molecules is based on assumptions, but the reasons is simply **because the statements based on these assumptions lead to predictions about atoms and molecules that agree with our observations.** Not just a few isolated observations over decades, millions of measurements on atoms and molecules have yielded data that agree with the conclusions based on the few postulates of quantum mechanics. With agreement between theory and experiment so abundant, the unproven postulates are accepted and no longer questioned. In the following discussion of the fundamentals of quantum mechanics, same of the statements may seem unusual or even contrary. However questionable they may seem at first, realize that **statements and equations based on these postulates agree with experiment and so constitute an appropriate model for the description of subatomic matter, especially electrons.**

Quantum mechanics is sometimes difficult at first glance, partly because **some new ideas and some new ways of thinking about matter are involved**. **Remember that the ultimate goal is to have a theory that proposes how matter behaves, and that predicts events that agree with observation**; that is, to have theory and experiment agree. Otherwise, a different theory is necessary to understand the experiment.

The main ideas are:

The behaviour of electrons, by now known to have wavelike properties can be described by a mathematical expression called a wavefunction.

The wavefunction contains within it all possible information that can be known about a system.

Wavefunctions are not arbitrary mathematical functions, but must satisfy certain simple conditions. For example, they must be continuous.

The most important condition is that the wavefunction must satisfy the time-dependent Schrodinger equation. With certain assumptions, time can be separated from the wavefunction, and what remains is a time-independent Schrodinger equation. We focus mainly on the time-independent Schrodinger equation. We focus mainly on the time-independent Schrodinger equation.

In the application of these conditions to real systems, wavefunctions are found that do indeed yield information that agrees with experimental observations of these systems: **quantum mechanics predicts values that agree with experimentally determined measurements**. To the extent that quantum mechanics not only reproduces their success but also extends it, quantum mechanics is superior to their **theories trying to describe the behaviour** of subatomic particles. **A proper understanding of quantum mechanics requires an understanding of the principles that it uses**.

On the basis of above discussion we may conclude that quantum mechanics properly, describes the behaviour of matter, as determined by observation.

Uncertainty principle:

Heisenberg's uncertainty principle states that product of the uncertainty in determining the position and momentum of the particle is approximately equal to a number of the other $\hbar$, where $\hbar = \frac{h}{2\pi}$, h being Planck's constant, i.e.

$$\Delta p\, \Delta q \simeq \hbar \qquad \text{... (1)}$$

where Δp is the uncertainty in determining the momentum and Δq is the uncertainty in determining the position of the particle. According to above relation the smaller is the value of Δq, i.e. more, exactly we can determine the position, the larger is the value of Δp, i.e. less excatly we can determine the momentum and vice-versa. The relation shows that it is impossible to determine simultaneously both the position and momentum of the particle accurately. Clearly this relation is fundamental since it sets a limit to the accurate and simultaneous measurements of position and momentum.

The relation is universal and holds for all the canonically conjugate physical quantities like position and momentum, eneryg and time, angular momentum and angle, etc. whose product has dimensions of action (joule-sec). Thus, if ΔE is the uncertainty in determining the energy of the system and Δt is the uncertainty in determining the time to which this determination refers, then we must have

$$\Delta E \Delta t \simeq \hbar \qquad \text{... (2)}$$

Similarly $$\Delta J \Delta \theta \simeq \hbar \qquad \text{... (3)}$$

where ΔJ is the uncertainty in determining the angular momentum and $\Delta \theta$ is the uncertainty in determining the angle. The exact statement of uncertainty principle is

The product of the uncertainties in determining the position and momentum of the particle can never be smaller than the number of order $\frac{1}{2}\hbar$.

So, the equation (1) takes the form

$$\Delta p\, \Delta q \geq \frac{1}{2}\hbar \qquad \text{... (4)}$$

Similarly equation (2) and (3) take the form

$$\Delta E \Delta t \geq \frac{1}{2}\hbar \qquad \text{... (5)}$$

And $$\Delta J \Delta \theta \geq \frac{1}{2}\hbar \qquad \text{... (6)}$$

Dual Nature of Light and matter :

It is well known that light exhibits the phenomena of interference, diffraction, polarisation, photoelectric effect, Compton effect and discrete emission and absorption of radiation. The phenomena of interference, diffraction and polarisation can only be explained on the basis of wave theory of light. These phenomena show that light possesses wave nature, on the other hand the phenomena of photoelectric effect, Compton effect and discrete emission and absorption of radiation can only be explained on the basis of quantum theory of light, according to the which light is propagated in small packets or bundles of energy $\hbar\omega$ or $h\nu$. These packetes are called photons or quanta and behave like corpuscles. Thus these latter phenomena indicate that light possesses corpuscular (or particle) nature. Thus we can say that light possesses dual nature. In some experiments it behaves as waves while in other experiments it behaves as particles.

IN 1923-24, de-Broglie proposed that the idea of dual nature (i.e. wave-particle duality) should be extended to all micro-particles, associating both wave and corpuscular characteristics with every particle. The experiments such as the those in which e/m of the material particles (electron, α -particle etc) is measured, indicate that the matter (i.e. material particles) possesses particle nature.

Matter wave:

Upto 1923 the matter was considered to be completely corpuscular in nature : but in that year Louis de-Broglie proposed that a material particle such as an electron, proton etc. might have a dual nature, just as ligh does. According to de-Broglie a moving particle, whatever its nature, has wave properties associated with it. de-Broglie proposed that the wavelength λ associated with any moving particle of momentum p (mass m and velocity v) is given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} \qquad \text{... (1)}$$

where, h is Planck's constant.

The wave assocaited with material particles are called the matter waves or de-Broglie waves. On the analogy of radiation the expression for the wavelenght λ can be easily derived.

The momentum of the photon $p = \frac{hc}{c} = \frac{h}{\lambda}$

Or, $$\lambda = \frac{h}{p} \qquad \text{... (6)}$$

Similarly, the wavelength of the waves associated with material particle is given by

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

The expression for the wavelength of the matter waves, as de-Broglie did, can also be derived using the general equation of a standing wave system and the principles of relativity.

Other expressions for de-Broglie wavelength:

The de-Broglie wavelength associated with a material particle of mass m and velocity v.

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

IF E_k is the kinetic energy of the material particle, then in non-relativistic ($v <<< c$) cases

$$p = \sqrt{(2mE_k)}$$

Therefore, de-Broglie wavelength of particle of K.E. = E_k is given by

$$\lambda = \frac{h}{\sqrt{(2mE_k)}}$$

If a charged particle carrying charge q is assocaited through a potential difference V volts, then kinetic energy $E_k = qV$.

Therefore, de-Broglie wavelength for charged particle of charge q and accelerated through a potential difference of V votls is

$$\lambda = \frac{h}{\sqrt{(2mqV)}}$$

When a material particle like neutron is in thermal equilibrium at temperature T, then they possess Maxwellian distribution of velocities and so the kinetic energy of most of material is given by

$$E_k = kT$$

where k is Boltzmann's constant $\left(k = 1.38 \times 10^{-23}\ joule/K\right)$

Therefore, the de-Broglie wavelength of a material particle at temperature T is

$$\lambda = \frac{h}{\sqrt{(2mE_k)}} = \frac{h}{\sqrt{(2mkT)}}$$

Photoelctric Effect:

During his experiments on e.m. waves in 1887, Hertz noticed that sparks occurred more rapidly in the air gap of the transmitter when an ultraviolet light is directed at one of the metal balls used in that experiment. Phillip Lenard, a student of Hertz studied the phenomena. He soon discovered that when the frequency of light is sufficiently high, electrons are emitted from the metal surface.

The phenomena in which electrons are emitted from the metal surface (e.g. Na, K, Cs etc.) when irradiated with light (photon) is called “Photo-electric effect”. The metals which exhibits this phenomena are called “Photo-sensitive materials” and the emitted electrons are called “Photo-electrons”. The existence of photo electric effect is not surprising. Light waves carry energy and some of the energy absorbed by the metal gets concentrated on a particular electron and reappear as their kinetic energy.

Lenard’s Experiment :

Lenard’s experimental arrangement is as shown in figure above. Two plane metal plates C and D are mounted in an evacuated tube. Plate G is coated with photosensitive metal and maintained at a negative whereas A another metal plate and kept at zero potential. The beam of negative ions emitted from C can pass through a hole in A. UV-radiation is incident on C through the quartz window W fitted to the side tube G and negative ions are emitted. These are attracted to A and a part of it passing through the hole in A is collated at D. The resulting electric current can be detected by an electrometer E.

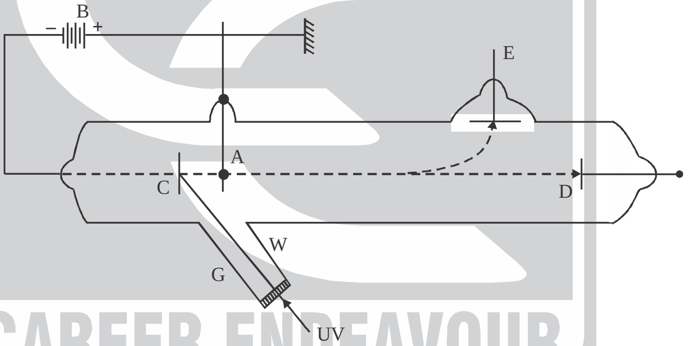

Figure : Experimental setup of Lenard’s experiment on photoelectric effect

If V be the potential difference between C and A, then the K.E. of the emitted negative ions is,

$$E_k = \frac{1}{2}mv^2 = eV$$

where, m is the mass of the ion and v is its velocity.

Further, if a positive potential is applied to C, the electric current is found to decrease with the increase of positive potential. Ultimately a stage comes when in a particular p.d. (V_s) the current becomes zero. Then, this V_s is called stopping potential. Electrons of all velocities up to the maximum v_m are stopped from reaching A. Then

$$E_{k,\,\max} = \frac{1}{2}mv_{\max}^2 = eV_s$$

Some experimental observations:

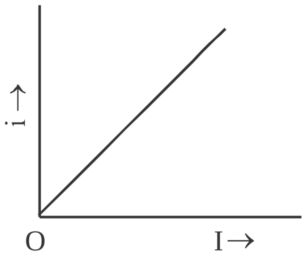

Figure : Variation of photo current (i) with the intensity of radiation (I)

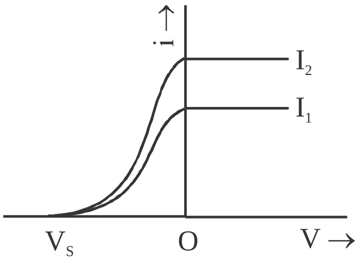

Figure : Variation of photo current (i) with Potential difference (V)

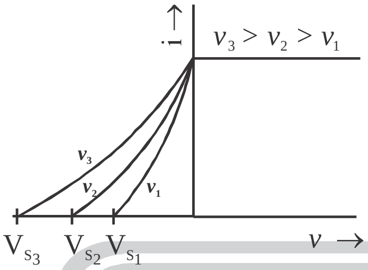

Figure : Plot of photocurrent (i) against Potential difference V showing the variation of stopping potential (V_s) with frequency (ν) of radiation.

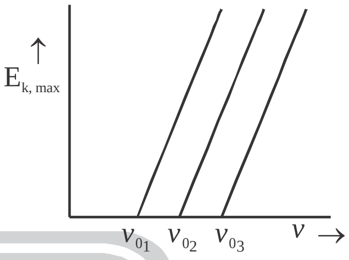

Figure : Plot of $E_{k,max}$ against ν.

(i) There is a certain minimum frequency ν_0 of incident radiation below which there is no emission of photo-electrons regardless of the intensity of the incident radiation. This frequency is known as threshold frequency which depends on the material and the nature of the emitting surface.

(ii) The maximum velocity or kinetic energy of the emitted photoelectrons depends on the frequency of the incident light, not on it's intensity i.e. blue light results in faster electrons than red light. The kinetic energy of the ejected electron increases linearly with incident frequency.

(iii) The emission of photo-electrons is instantaneous i.e. no time interval between arrival of light at the metal surface and emission of photo-electrons, no matter how feeble the incident light is.

(iv) At a fixed frequency, the number of ejected electrons increases with the intensity of the light but does not depend on its frequency.

Failures of Classical E.M. theory:

(i) According to wave theory, photo-electric emission should occur for any frequency of light, no concept of threshold frequency.

(ii) According to wave theory, the energy of the incident light is distributed over the entire wave front. So, electrons will take some time to eject from the surface i.e. no concept of instantaneous emission.

(iii) The electric field and magnetic field of the incident light wave exert forces to liberate electrons from the metal surface. So, the light of higher intensity consists of stronger fields and should give higher velocity to the photoelectrons.

Einstein's hypothesis:

(i) The emission and absorption of radiation takes place in descrete quanta of energy $\varepsilon = h\nu$.

(ii) Energy in light is not spread out over the entire wavefront but is concentrated in small packets known as 'photons'. The incident photon on the metal surface can transfer the whole energy to one electron without any time lag.

(iii) A certain minimum energy called the work function W_0 is required to release an electron from the metal surface.

Photo-electric equation:

When a radiation of frequency ν is incident on the metal surface in vaccum, it can be either be reflected from the metal surface or it can be completely absorbed by an electron. In the second case, the electron can be knocked out of the surface. The emission of electron from the metal surface is possible only if $h\nu > W_0$. The remaining energy $\left(h\nu - W_0\right)$ can be utilized to impart kinetic energy of the emitted electrons.

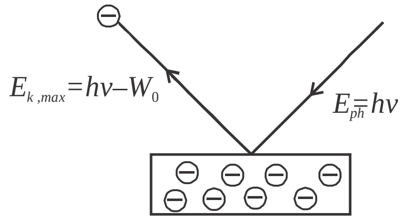

Figure : Mechanism of Photoelectric effect.

So, the maximum kinetic energy of the emitted electrons is

$$E_{k,\max} = \frac{1}{2}mv_{\max}^2 = h\nu - W_0 = h\nu - h\nu_0$$

where '*m*' is the rest mass of the electron, $v_{\max}$ is the maximum velocity of the emitted electrons and ν_0 is the threshold frequency. This is the well-known Einstein's photo-electric equation.

Explaination of Photoelectric effect:

(i) If $\nu < \nu_0$, the maximum kinetic energy of the emitted photo-elctron is negative. This means that no electrons could be emiited if the frequency of the incident photon ν is less than the threshold frequency ν_0.

(ii) Above the threshold frequency, the maximum kinetic energy of the emitted photoelectrons varies linearly with ν, it does not depend on the intensity of the incident radiation.

(iii) An increase in the frequency of the incident radiation for a fixed frequency ν, is equivalent to the increase in the number of photon and not energy.

(iv) Above the threshold frequency, the incident photon is absorbed at an instant by the electron and is emitted instantaneously.

SOLVED PROBLEMS

1. Electron are accelerated through 344 volts and are reflected from acrystal the first reflection maximum occur when glancing angle 60ºC. Determine the spacing of the crystal.

Soln. $n\lambda = 2d\sin\theta$

$$\lambda = \frac{h}{\sqrt{2meV}} = \frac{6.6\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times1.6\times10^{-19}\times344}} = 6.6\times10^{-11}$$

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

$$1\times6.6\times10^{-11} = 2\times d\times\frac{\sqrt{3}}{2} \quad\Rightarrow\quad d = 0.5\mathring{A}$$

2. A beam of mono energestic neutrons corresponding 207ºC falls on a crystal. First order reflection is observed at a glancy angle 30º. What is interplanar space.

Soln. $$\lambda = \frac{h}{\sqrt{2mkT}} = \frac{6.6\times10^{-34}}{\sqrt{2\times1.6\times10^{-27}\times1.38\times10^{-23}\times48}} = 1.4\mathring{A}$$

$$2d\sin30 = \lambda \quad\Rightarrow 2d\times\frac{1}{2} = 1.4\mathring{A} \qquad\Rightarrow\ d = 1.4\mathring{A}$$

3. Calculate the wavelength of thermal neutron at 27°C

Soln. $$\lambda = \frac{6.6\times10^{-34}}{\sqrt{2\times1.6\times10^{-27}\times1.38\times10^{-23}\times300}} = 1.7\text{Å}$$

4. Show that the de-Broglie wavelength λ associated with moving electron is the $\lambda = \frac{12.28}{\sqrt{v}}$.

Soln. $$\lambda = \frac{h}{\sqrt{2\,m\times e}\sqrt{v}} = \frac{6.6\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times1.6\times10^{-29}}\sqrt{v}} = \frac{12.28}{\sqrt{v}}\text{Å}$$

Heisenberg uncertainty Principle:

$$\Delta x\Delta p_x \ge \frac{\hbar}{2};\quad \Delta x\Delta p_x \ge \frac{h}{4\pi};\ \Delta E\ \Delta t \ge \frac{\hbar}{2};\ \Delta E\ \Delta t \ge \frac{h}{4\pi};\ \Delta J\ \Delta\phi \ge \frac{\hbar}{2};\ \Delta J\ \Delta\phi \ge \frac{h}{4\pi}$$

ΔJ is the uncertainty angular movement $\Delta\phi$ is the uncertainty in the corresponding angle.

5. An a electron has a speed of 50 cm/sec with an accuracy of 0.005%. Calculate the uncertainty with which we can locate the position of electron.

Soln. Since, we know that, $\Delta x\ \Delta p_x = \frac{h}{4\pi} \Rightarrow \Delta x\times m\text{v} = \frac{h}{4\pi}$

$$\Rightarrow \Delta x = \frac{h}{4\pi m\text{v}} = \frac{6.6\times10^{-34}}{4\times3.14\times9.1\times10^{-31}\times50\times0.005} = 2.3\times10^{-3}m \qquad \left(\because\ h = 6.6\times10^{-34}\right)$$

6. The average time that an atom retains before re-emiting in the form of electromagnetic radiation is 10^{-8} second. Calculate the limit of accuracy of excitation energy.

Soln. $$\Delta E\ \Delta t = \frac{h}{4\pi}$$

$$\Delta E = \frac{6.6\times10^{-34}}{4\times3.14\times10^{-8}} = 0.54\times10^{-26}\,Joule\ = \frac{5.4\times10^{-27}}{1.6\times10^{-19}}\,Joule = 3\times10^{-8}\,eV$$

7. If a component of a angular momentum of the electron in a H atom is known to be $2\hbar$ with 5% energy, the angular orbitals in the terms of angle.

Soln. $$\Delta J\ \Delta\phi = \frac{h}{4\pi}$$

$$\Delta J = \frac{2\hbar\times5}{100} = \frac{10\hbar}{100} = \frac{\hbar}{10} = \frac{\hbar}{20\pi}$$

$$\Delta J = \frac{h}{20\pi}$$

$$\frac{h}{20\pi}\times\Delta\phi = \frac{h}{4\pi}$$

$$\Delta\phi = 5^\circ$$

8. Calculate the de-Broglie wavelength of an electron having a kinetic energy of 1000eV. Compare the result with the wavelength of x-rays having the same energy.

Soln. The kinetic energy,

$$T = \frac{p^2}{2m} = 1000eV = 1.6\times10^{-16}\,J$$

$$\lambda = \frac{h}{p} = \frac{6.626\times10^{-34}\,js}{\left[2\times\left(9.11\times10^{-31}kg\right)\times\left(1.6\times10^{-16}J\right)^{1/2}\right]}$$

$$= 0.39\times10^{-10}m = 0.39\text{Å}$$

For x-rays, energy $= \dfrac{hc}{\lambda}$

$$\lambda = \frac{\left(6.626\times10^{-34}\,Js\right)\times\left(3\times10^{8}\,m/s\right)}{1.6\times10^{-16}J} = 12.42\times10^{-10}m = 12.42\text{Å}$$

$$\frac{\text{wavelength of x-rays}}{\text{de-Broglie wavelength of electron}} = \frac{12.42\text{Å}}{0.39\text{Å}} = 31.85$$

9. What is the de-Broglie wavelength of an electron that has been accelerated through a potential difference of 100V? **[TIFR 2014]**

(a) 0.123 nm (b) 0.123Å (c) 1.23×10^{-11} cm (d) none of the above

Soln. The energy gained by the electron = 100 eV. Then,

$$\frac{p^2}{2m} = 100eV = \left(100\,eV\right)\left(1.6\times10^{-19}\,J/eV\right)$$

$$p = \left[2\left(9.1\times10^{-13}kg\right)\left(1.6\times10^{-17}J\right)\right]^{1/2} = 5.396\times10^{-24}kg\,ms^{-1}$$

$$\lambda = \frac{h}{p} = 200\,eV = 3.2\times10^{-17}J = 1.23\times10^{-10}m = 1.13\text{Å} = 0.123\,nm$$

Correct answer is (a)

10. Determine the de-Broglie wavelength of an electron that has been accelerated through a potential difference of 200 V.

Soln. The energy gained by the electron = 200 eV. Then,

$$\frac{p^2}{2m} = 200eV = 3.2\times10^{-17}J$$

$$p = \left[2\left(9.1\times10^{-31}kg\right)\left(3.2\times10^{-17}J\right)\right]^{1/2} = 7.632\times10^{-24}\,kgms^{-1}$$

$$\lambda = \frac{h}{p} = \frac{6.626\times10^{-34}\,Js}{7.632\times10^{-24}kg\,ms^{-1}} = 0.868\times10^{-10}m = 0.868\text{Å}$$

11. Estimate the velocity of neutrons needed for the study of neutron diffraction of crystal structures if the inter-atomic spacing in the crystal is of the order of 2Å. Also estimate the kinetic energy of the neutrons corresponding to this velocity. Mass of neutron = 1.6749×10^{-27} kg.

Soln. de-Broglie wavelength

$$\lambda \cong 2\times10^{-10}m$$

$$\Rightarrow \quad \lambda = \frac{h}{mv} \text{ or } v = \frac{h}{m\lambda}$$

$$\Rightarrow \quad \text{v} = \frac{6.626\times10^{-34}\,Js}{\left(1.6749\times10^{-27}kg\right)\left(2\times10^{-10}m/s\right)} = 1.978\times10^{3}\,ms^{-1}$$

$$\text{Kinetic energy, } T=\frac{1}{2}mv^2=\frac{1}{2}\left(1.6749\times10^{-27}\,kg\right)\left(1.978\times10^{3}\ ms^{-1}\right)^2$$

$$=3.2765\times10^{-21}\,J=20.478\times10^{-3}\ eV$$

12. What is the ratio of the kinetic energy of an electron to that of a proton if their de-Broglie wavelength are equal?

Soln. m_1 = mass of electron, m_2 = mass of proton
v_1 = velocity of electron, v_2 = velocity of proton.

$$\lambda=\frac{h}{m_1\text{v}_1}=\frac{h}{m_2\text{v}_2}\qquad\text{or}\qquad m_1\text{v}_1=m_2\text{v}_2$$

$$m_1\left(\frac{1}{2}m_1\text{v}_1^2\right)=m_2\left(\frac{1}{2}m_2\text{v}_2^2\right)\quad\Rightarrow\quad\frac{\frac{1}{2}m_1v_1^2}{\frac{1}{2}m_2v_2^2}=\frac{m_2}{m_1}$$

$$\frac{\text{kinetic energy of electron}}{\text{Kinetic energy of proton}}=\frac{m_2}{m_1}=1836$$

13. An electron has a speed of 500 m/s with an accuracy of 0.004%. Calculate the certainty with which we can locate the position of the electron.

Soln. Momentum p = mv = $(9.11\times10^{-31}\text{kg})\times(500\text{ m/s})$

$$\frac{\Delta p}{p}\times100=0.004$$

$$\Delta p=\frac{0.004\left(9.11\times10^{-31}\,kg\right)\left(500\ m/s\right)}{100}=182.2\times10^{-34}\,kgm\ s^{-1}$$

$$\Delta x\cong\frac{h}{\Delta p}=\frac{6.626\times10^{-34}\,Js}{182.2\times10^{-34}\,kgms^{-1}}=0.0364m$$

The position of electron cannot be measured to accuracy less than 0.036m.

14. The average lifetime of an excited atomic state is 10^{-9}s. If the spectral line associated with the decay of this state is 6000Å, estimate the width of the line.

Soln. $\Delta t=10^{-9}\ s,\qquad \lambda=6000\times10^{-10}\,m=6\times10^{-7}\,m$

$$E=\frac{hc}{\lambda}\ \text{or}\ \Delta E=\frac{hc}{\lambda^2}\Delta\lambda\ \Rightarrow\Delta E.\Delta t=\frac{hc}{\lambda^2}\Delta\lambda.\Delta t=\frac{\hbar}{2}=\frac{h}{4\pi}$$

$$\Delta\lambda=\frac{\lambda^2}{4\pi c\Delta t}=\frac{36\times10^{-14}\,m^2}{4\pi\left(3\times10^{8}\ m/s\right)\times\left(10^{-9}\,s\right)}=9.5\times10^{-14}\,m$$

15. An electron in the n = 2 state hydrogen remains there on the average of about 10^{-8} s, before makin a transition to n = 1 state
(i) estimate the uncertainty in the energy of the n = 2 state
(ii) what fraction of the transition energy is this?
(iii) what is the wavelength and width of this line in the spectrum of hydrogen atom?

Soln. (i) $\Delta E\geq\frac{h}{4\pi\Delta t}=\frac{6.626\times10^{-34}\,Js}{4\pi\times10^{-8}\,s}==-13.6\,eV0.527\times10^{-26}\,J=3.29\times10^{-8}\ eV$

(ii) Energy of $n=2\rightarrow n=1$ transition

$$=-13.6\,eV\left(\frac{1}{2^2}-\frac{1}{1^2}\right)=10.2\,eV$$

$$\text{Fraction }\frac{\Delta E}{E}=\frac{3.29\times10^{-8}\,eV}{10.2\,eV}=3.23\times10^{-9}$$

(iii) $\lambda=\dfrac{hc}{E}=\dfrac{\left(6.626\times10^{-34}\,Js\right)\times\left(3\times10^{8}\,m/s\right)}{\left(10.2\times1.6\times10^{-19}\,J\right)}=1.218\times10^{-7}\,m=122\,nm$

$$\frac{\Delta E}{E}=\frac{\Delta\lambda}{\lambda}\quad\text{or}\quad\Delta\lambda=\frac{\Delta E}{E}\times\lambda$$

$$\Delta\lambda=\left(3.23\times10^{-9}\right)\left(1.218\times10^{-7}\,m\right)\;=3.93\times10^{-16}\,m=3.93\times10^{-7}\,nm$$

16. If the position of a 5 k eV electron is located within 2Å, what is the percentage uncertainty in its momentum?

Soln. $\Delta x=2\times10^{-10}\,m;\;\Delta p.\Delta x\cong\dfrac{h}{4\pi}$

$$\Delta p\cong\frac{h}{4\pi\Delta x}=\frac{\left(6.626\times10^{-34}\,Js\right)}{4\pi\left(2\times10^{-10}\,m\right)}=2.635\times10^{-25}\,kg\;ms^{-1}$$

$$p=\sqrt{2mE}=\left(2\times9.11\times10^{-31}\times5000\times1.6\times10^{-19}\right)^{1/2}=\;3.818\times10^{-23}\,kg\;m\;s^{-1}$$

$$\text{Percentage of uncertainty}=\frac{\Delta p}{p}\times100=\frac{2.635\times10^{-25}}{3.818\times10^{-23}}\times100=0.69$$

17. The uncertainty in the velocity of a particle is equal to its velocity. if $\Delta p.\Delta x\cong h$, show that the uncertainty in its location is its de-Broglie wavelength.

Soln. Given $\Delta v=v$. Then,

$$\Delta p=m\Delta v=mv=p$$

$$\Delta x\times\Delta p\cong h\quad\text{or}\quad\Delta x.p\cong h$$

$$\Delta x\cong\frac{h}{p}=\lambda$$

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

Soln. The wavelength λ of visible light is in the range 4000–7000 Å. Then,

$$\text{Energy of 4000Å light }=\frac{hc}{\lambda}=\frac{\left(6.626\times10^{-34}\,Js\right)\left(3\times10^{-8}\,m/s\right)}{\left(4000\times10^{-10}\,m\right)\left(1.6\times10^{-19}\,J/eV\right)}=3.106\,eV$$

$$\text{Energy of 7000Å light}=\frac{6.626\times10^{-34}\times3\times10^{8}}{7000\times10^{-10}\times1.6\times10^{-19}}=1.77\,eV$$

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.

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

Soln. The energy of the radiation having wavelength 2000Å is obtained as

$$\frac{hc}{\lambda}=\frac{\left(6.626\times10^{-34}\,Js\right)\left(3\times10^{8}\ m/s\right)}{\left(2000\times10^{-10}m\right)\left(1.6\times10^{-19}\ J/eV\right)}=6.212\,eV$$

Work function = 4.2 eV

KE of fastest electron = 6.212 – 4.2 = 2.012 eV

Stopping potential = 2.012 V

Threshold wavelength $\lambda_0=\dfrac{hc}{\text{work function}}$

$$\lambda_0=\frac{\left(6.626\times10^{-34}\,Js\right)\left(3\times10^{8}\ m/s\right)}{\left(475\times10^{-9}m\right)\left(1.6\times10^{-19}\ J/eV\right)}=2.62\,eV$$

Stopping potential = 2.62–2.14 = 0.48 V

20. An electron accelerated through a potential difference of φ volts impinges on a nickel surface, whose (100) planes have a spacing $d=351.5\times10^{-12}m\left(351.5\ pm\right)$. The **de-Broglie** wavelength of the electron is $\dfrac{\lambda}{pm}=\left(\dfrac{a}{\varphi}\right)^{1/2}$. The value of 'a' in volts is **[GATE 2008]**

(a) 1.5×10^{-18} (b) 1.5×10^{6} (c) 6.63×10^{-5} (d) 2.5×10^{18}

Soln. Given, $\dfrac{\lambda}{pm}=\left(\dfrac{a}{\varphi}\right)^{1/2}$ ... (1)

$$\frac{\lambda^2}{(pm)^2}=\frac{a}{\varphi}$$

Or, $a=\varphi\dfrac{\lambda^2}{(pm)^2}$

From equation (1),

Or, $\dfrac{h}{\sqrt{2meV}\,(pm)}=\left(\dfrac{a}{\varphi}\right)^{1/2}$

$$\Rightarrow\quad \frac{6.6\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times1.6\times10^{-19}\varphi}\,(pm)}=\frac{(a)^{1/2}}{(\varphi)^{1/2}}$$

$$\Rightarrow\quad \frac{6.6\times10^{-34}}{\sqrt{29.12\times10^{-50}}\,(pm)}=(a)^{1/2}\qquad\left[\begin{array}{l}\because\ 351.5\times10^{-12}m=351.5\ pm\\ 1\ pm=1\times10^{-12}m\end{array}\right]$$

$$\Rightarrow\quad \frac{\left(6.6\times10^{-34}\right)\left(6.6\times10^{-34}\right)}{29.12\times10^{-50}\times(pm)^2}=a\quad\Rightarrow\frac{43.56\times10^{-68}}{29.12\times10^{-50}\times10^{-12}\times10^{-12}}=a$$

$\therefore\quad a=1.5\times10^{6}$

Correct option is (b)

21. If Δy and ΔP_y are the uncertainties in the y-coordinate and the y component of the momentum of a particle respectively, then, according to uncertainty principle $\Delta y \Delta P_y$ is: $\left(\hbar = \frac{h}{2\pi} \text{ and h is Planck's constant}\right)$

(a) $\geq \hbar$ (b) $> \hbar/2$ (c) $> \hbar$ (d) $\geq \hbar/2$ **[GATE 2012]**

Soln. Since, we know that,

Uncertainity principle, $\Delta y\, \Delta p_y \geq \frac{\hbar}{2}$

Correct option is (d)

Concept of Wavefunction

Quantum mechanics acknowledges the wave-particle duality of matter and the existence of quantization by supposing that, rather than travelling along a definite path, a particle is distributed through space like a wave. The mathematical representation of the wave that in quantum mechanics replaces the classical concept of trajectory is called a wavefunction, (ψ) (*psi*). The Schrodinger equation is a second-order differential equation used to calculate the wavefunction of a system.

The Schrodinger equation:

For one-dimensional systems.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi=E\psi$$

where $V(x)$ is the potential energy of the particle and E is its total energy. For three-dimensional systems.

$$-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi$$

where V may depend on position and ∇^2 (del square) is

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

In the general case the Schrodinger equation is written

$$\hat{H}\psi=E\psi$$

where $\hat{H}$ is the hamiltonian operator for the system:

$$\hat{H}=-\frac{\hbar^2}{2m}\nabla^2+V$$

For the evolution of a system with time, it is necessary to solve the time-dependent Schrodinger equation:

$$\hat{H}\psi=i\hbar\frac{\partial\psi}{\partial t}$$

A central principle of quantum mechanics is that the wavefunction contains all the dynamical information about the system it describes. Here we concentrate on the information it carries about the location of the particle.

The interpretation of the wavefunction in terms of the location of the particle is based on a suggestion made by ***Max Born***. He made use of an analogy with the wave theory of light, in which the square of the amplitude of an electromagnetic wave in a region is interpreted as its intensity and therefore (in quantum terms) as a measure of the probability of finding a photon present in the region. The Born interpretation of the wavefunction focuses on the square of the wavefunction.

If the wavefunction of a particle has the value $\psi(x)$ at some point *x*, then the probability of finding the particle between x and (x + dx) is proportional to $|\psi_x|^2\,dx$.

Thus, $|\psi_x|^2$ is the probability density, and to obtain the probability it must be multiplied by the length of the infinitesimal region dx. The wavefunction $\psi(x)$ itself is called the **probability amplitude**.

For a particle free to move in three dimensions (for example, an electron near a nucleus in an atom), the wavefunction depends on the point ‘r’ with coordinates x, y and z, and the interpretation of $\psi(r)$ is as follows. If the wavefunction of a particle has the value ψ at some point ‘r’, then the probability of finding the particle in an infinitesimal volume $d\tau=dxdydz$ at that point is proportional to $|\psi|^2\,d\tau$.

The square of a wavefunction is a probability density, and (in three dimensions) has the dimensions of 1/length^3. It becomes a (unitless) probability when multiplied by a volume. In general, we have to take the account the variation of the amplitude of the wavefunction over the volume of interest, but here we are supposing that the volume is so small that the variation of ψ in the region can be ignored.

Mathematical feature of the Schrodinger equation is that, if ψ is a solution, then so is $N\psi$, where N is any constant. This freedom to vary the wavefunction by a constant factor means that it is always possible to find a normalization constant, N, such that the proportionality of the Born interpretation becomes an equality.

We find the normalization constant by noting that, for a normalized wavefunction $N\psi$ the probability that a particle is in the region dx is equal to $(N\psi)(N\psi)dx$ (we are taking N to be real). Furthermore, the sum over all space of these individual probabilities must be 1.
The integration is over all the space accessible to the particle. For systems with spherical symmetry it is best to work in spherical polar coordinates r, θ and ϕ.

$$x = r\sin\theta\cos\phi,\;\; y = r\sin\theta\sin\phi,\;\; z = r\cos\theta$$

r, the radius, ranges from 0 to ∞

θ, the colatitude, ranges from 0 to π

ϕ, the azimuth, ranges from 0 to 2π

Standard manipulation then yield.

$$d\tau = r^2\sin\theta dr d\theta d\phi$$

Interpretation of the ψ functions:

The eigenfunction ψ is by nature a sort of amplitude function. In the case of a light wave, the intensity of the light or energy of the electromagnetic field at any point is proportional to the square of the amplitude of the wave at that point. From the point of view of the photon picture, the more intense the light at any place, the more photons are falling on that place. This fact can be expressed in another way by saying that the greater is the probability of a photon being within that region.

It is this interpretation that is most useful when applied to the eigenfunctions of Schrodinger's equation. They are therefore sometimes called **probability amplitude functions**. If $\psi(x)$ is a solution of the wave equation for an electron, then the probability of finding the electron within the range from x to $x + dx$ is given by $|\psi|^2 dx$.

The physical interpretation of the eigenfunction as a probability amplitude function is reflected in certain mathematical conditions that it must obey. It is required that $\psi(x)$ be single-valued, finite, and continuous for all physically possible values of x must have one and only one value. It cannot be infinite at any point, for then the electron would be fixed at exactly that point, which would be inconsistent with the wave properties. The requirement of continuity is helpful in the selection of physically reasonable solutions for the wave equation.

Since the function ψ may be a complex quantity, the probability is written more generally as $\psi^*\psi$, where ψ^* is the complex conjugate of ψ. Thus, e.g., if $\psi = e^{-ix}$, $\psi^* = e^{ix}$.

The probabilistics nature of quantum mechanics disturbed many physicists, including Einstein, Schrodinger, and de-Broglie, (Einstein wrote in 1926: "Quantum mechanics says a lot, but does not really bring us any closer to the secret of the Old One. I, at any rate, am convinced that he does not throw dice." When someone pointed out to Einstein that Einstein himself had introduced probability into quantum theory when he interpreted a light wave's intensity in each small region of space as being proportional to the probability of finding a photon in that region, Einstein replied, "A good joke should not repeated too often". These scientists believed that quantum mechanics does not furnish a complete description of physical reality. However, attempts to replace quantum mechanics by an underlying deterministics theory have failed. There appears to be a fundamental randomness in nature at the microscopic level.