investigated some of the consequences of relativity theory. For electromagnetic radiation, لنا ع النظرية النسبية

$$E = h\upsilon = \frac{hc}{\lambda} \quad \ldots\ldots 9$$

Where C, v, and λ are the velocity, frequency, and wavelength, respectively, for the radiation. The photon also has an energy given by the relationship from relativity theory, طاقة الفوتون تعطى بمعادلة

$$E = mC^2 \quad \ldots\ldots 29$$

A particular photon has only one energy, so

$$mc^2 = \frac{hc}{\lambda} \quad \ldots\ldots 30$$

Which can be written as:

$$\lambda = \frac{h}{mc} \quad \ldots\ldots 31$$

This does not mean that light has a mass, but because mass and energy can be interconverted, it has an energy that is equivalent to some mass. The quantity represented as mass time's velocity is the momentum, so Eq 31predicts a wavelength that is Planck's constant divided by the momentum. De Broglie reasoned that if a particle had a wave character, the wavelength would be given by

$$\lambda = \frac{h}{mv} \quad \ldots\ldots 32$$

Where the velocity is written as v rather than c because the particle will not be traveling at the speed of light. This was verified in 1927 by C. J. Davisson and L. H. Germer working at Bell Laboratories in Murray Hill, New Jersey. In their experiment, an electron beam was directed at a metal crystal and a diffraction pattern was observed. Since diffraction is a property of waves, it was concluded that the moving electrons were behaving as waves. The reason for using a metal crystal is that in order to observe a diffraction pattern, the waves must pass through openings about the same size as the wavelength, and that distance corresponds to the distance separating atoms in a metal. The de Broglie wavelength of moving particles (electrons particularly) has been verified experimentally. This is, of course, important, but the real value is that electron diffraction has now become a standard technique for determining molecular structure.

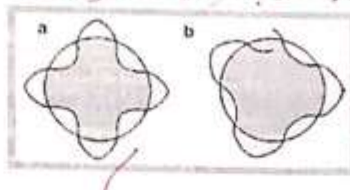

Figure 9: (a) An allowed orbit containing a whole number of wavelengths and (b) an unstable orbit.

In developing a model for the hydrogen atom, Bohr had to assume that the stable orbits were those where

$$mvr = n\frac{h}{2\pi} \quad \ldots\ldots 33$$

Because de Broglie showed that the moving electron should be considered as a wave, that wave will be a stable one only if the wave joins smoothly on itself. This means that the circular orbit must contain a whole number of wavelengths as in Figure 9. The circumference of a circle in terms of the radius, r, is $C = 2\pi r$. Therefore, a whole number of wavelengths, $n\lambda$, must be equal to the circumference:

$$2\pi r = n\lambda \quad \ldots\ldots 34$$

However, the de Broglie wavelength, λ, is given by

$$\lambda = \frac{h}{mv} \quad \ldots\ldots 35$$

$$2\pi r = n\frac{h}{mv} \quad \ldots\ldots 36$$

Which can be rearranged to give

$$mvr = n\frac{h}{2\pi} \quad \ldots\ldots 33$$

Which is exactly the same as the equation that Bohr assumed in order to predict which orbits were stable! We now see the connection between the wave character of a particle and the Bohr model. Only two years later, Erwin Schrödinger used the model of a standing wave to represent the electron in the hydrogen atom and solved the resulting wave equation. ~~We will describe this monumental event in science later~~. While the Bohr model explained the spectral properties of the hydrogen atom, it did not do so for any other atoms. However, He^{+}, Li^{2+}, and similar species containing one electron could be treated by the same model by making use of the appropriate nuclear charge. Also, the model considered the atom almost like a mechanical device, but since the atom did not radiate energy continuously, it violated laws of electricity and magnetism.

The Heisenberg Uncertainty Principle

A serious problem with the Bohr model stems from the fact that it is impossible to know simultaneously the position and momentum (or energy) of a particle. A rationale for this can be given as follows. Suppose you observe a ship and determine its position. The visible light waves have a wavelength of about 4×10^{-5} to 8×10^{-5}cm (4×10^{-7} to 8×10^{-7}m) and very low energy. The light strikes the ship and is reflected to your eyes, the detector. Because of the very low energy of the light, the ship, weighing several thousand tons, does not move as a result of light striking it. Now, suppose you wish to "see" a very small particle of perhaps 10 cm (10^{-10}m) diameter. In order to locate the particle you must use "light" having a wavelength about the same length as the size of the particle. Radiation of 10^{-8} cm (very short) wavelength has very high energy since

$$E = \frac{hc}{\lambda} \qquad (37)$$

Therefore, in the process of locating (observing) the particle with high-energy radiation, we have changed its momentum and energy. Therefore, it is impossible to determine both the position and the momentum simultaneously to greater accuracy than some fundamental quantity. That quantity is h and the relationship between the uncertainty in position (distance) and that in momentum (mass × distance/time) is

$$\Delta x . \Delta(mv) \geq \hbar/2 \ \ \text{or} \ \ \frac{h}{4\pi} \qquad (38)$$

This relationship, which is one form of the Heisenberg uncertainty principle, indicates that h is the fundamental quantum of action. We can see that this equation is dimensionally correct since the uncertainty in position multiplied by the uncertainty in momentum has the dimensions of

$$distance \times \left(mass \times \frac{distance}{time}\right) \text{ In cgs units, } cm \times \left(g \times \frac{cm}{s}\right) = erg.S$$

And the units of erg s match the units on h. If we use uncertainty in time in seconds and uncertainty in energy is erg s,

$$\Delta t . \Delta E \geq \hbar/2 \qquad (39)$$

And this equation is also dimensionally correct. Therefore, an equation of this form can be written between any two variables that reduce to erg s or g cm² /s. It is implied by the Bohr model that we can know the details of the orbital motion of the electron and its energy at the same time. Having now shown that is not true, we will direct our attention to the wave model of the hydrogen atom.

$erg.s = g\ cm^2/s$

Sommerfeld quantization:

Bohr interpreted the formation of line spectra of hydrogen atom but not the fine structure. Thus, Bohr failed in his postulate which include that an electron is rotate around the nucleus by a constant circular orbit where, the moment and the position of the certain electron can be determined accurately at same time but, this case is contrast with the uncertainty principle where, if the moment is calculated in exactly, the calculation of the position then is approximately. Sommerfeld and Wilson at 1915 found a new method for the quantization in order to interpret the fine structure of hydrogen atom and helium ion that include two respects:

1. Solving the kinetic equations according to the classical mechanics by using Hamilton's function by using the coordinates and the moment as independent variables.
2. The equation that obey to the quantum condition is taken into account among all the above kinetic equations.

For instance, if any system include f of the degree of variation, the quantum condition is:

$$\oint p_i dq_i = nh \quad \text{.......... 1}$$

Where, q_i is the coordinates and p_i is the momentum. The symbol $\oint p_i$ represent the integration of complete periodic motion i.e., it repeated in a systematic periodic. The non-periodic motion is not obey to the quantum condition because it is not quantized i.e., it is not behave as multiple for a constant quantum. n in equation 1 is the quantum number which is natural number in most cases but sometimes a half quantum number can be used i.e., n can be take a series of 1/2, 3/2, 5/2, …etc. in this case there are many quantized motion for the particular system and the energy of these motions are called as energy levels. On the other hands, these energies can be substituted in the following equation in order to estimate the frequency for the system:

$$\nu = \frac{E_1 - E_2}{h} \quad \text{.......... 2}$$

Sommerfeld instead that the orbital is elliptical but not circular according to use the quantum condition. An important applications for Sommerfeld rules (quantum condition) the estimation of energy levels of harmonic oscillators, rigid rotators and particle in a box.

Quantum Mechanics:

Quantum mechanics is one of the systems that described by two different methods the first, by Werner Heisenberg and the second by Schrödinger. Then Paul Dirac insisted that both of them are same. Thus, three methods can describe the quantum mechanics:

1. *Heisenberg representation:*

Heisenberg used the mathematical matrices to define the quantum mechanics, the matrix then is called matrix mechanics where, the system is represented by an oriented (column of the matrix) and each variable dynamics' is accompanied by a matrix. The information are obtained by solving the mentioned matrices.

2. *Schrödinger representation :*

According to Debrogli the difficulties in Bohr's theory can be solved by writing a wave equation for the mater. Schrödinger advantaged from the concepts of Debrogli and writing his famous equation for the matter. His study that depend on the wave is called as wave mechanics.

3. *Dirac representation:*

Dirac explained that both of Heisenberg and Schrödinger representations are in same case. He represented the system in a mathematical function is called *(Ket)* which is referred by the symbol $|i\rangle$ where, i represent the certain case for the mentioned function. The conjugation of this function is called *(bra)* that referred by the symbol $\langle j|$. He is using the mathematic operator to describe the empirical measurements where, this operator depends upon the physical state for the system. He is solving the mathematical equations that represent the particular system according to exchange law for calculation of the energy of the harmonic oscillator.

Schrödinger Equation:

According to the laboratory experiments, the particle has a wave property. Hence, the wave motion can be expressed by the function is called ψ. The suitable and simple formula to express the mentioned function is sine wave as in below:

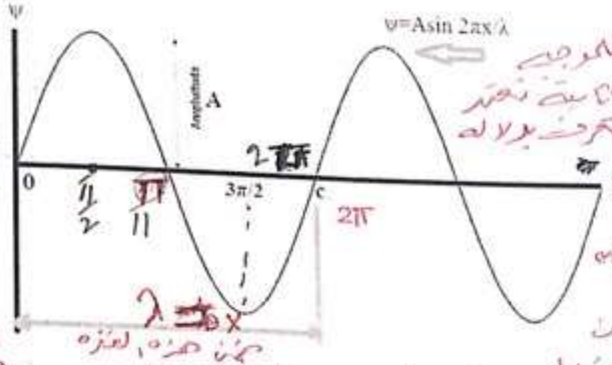

Figure 1: Sine wave function.

The wave function ψ can be expressed by the following equation:

$$\psi = A \sin bx \quad \text{.......................................3}$$

Where A is the amplitude i.e., the maxima of the wave, b is the constant that depend on the wave in question which can be expressed by the wave length λ. To find the value of b we assumed that the value of the wave should be equaled to zero then ψ is zero at this point. The function is in maximum value when bx =π/2 then it equal to one when bx=π but it has a minimum value when bx=3π/2 then equal to zero at bx=2π. The distance between zero and 2π is equivalent to one λ. Hence:

$bx = 2\pi \rightarrow x = \lambda \rightarrow b = \frac{2\pi}{\lambda}$ Substitution of b value in equation 3:

$$\psi = A \sin \frac{2\pi}{\lambda} x \quad \text{.......................................4}$$

Equation 4 represent the value of sine wave as a function of the wave length λ. On the other hand, the wave function ψ can be represented as a cosin wave as in equation 5:

$$\psi = B \cos \frac{2\pi}{\lambda} x \quad \text{.......................................5}$$

Generally, the wave function ψ can be represented by the summation of equations 4 & 5:

$$\psi = A \sin \frac{2\pi}{\lambda} x + B \cos \frac{2\pi}{\lambda} x \quad \text{.......................................6}$$

The aim of the referring to the wave motion is to link between the quantum theory and this motion. Double differential for equation 6:

$$\frac{d^2\psi}{dx^2} = \frac{-4\pi^2}{\lambda^2}\left[A \sin \frac{2\pi}{\lambda} x + B \cos \frac{2\pi}{\lambda} x \right] \text{.......................................7}$$

Substitution of ψ in equation 6 to equation 7:

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2\psi}{\lambda^2} = 0 \quad \ldots\ldots 8$$

Equation 8 will be applied in quantum mechanics. As equation 8 derived from the classical wave motion where it assumed that the particle has the wave property according to Debrogli. Thus, equation 8 can be applied on the matter when the value of wave length is λ in Debrogli by the linear momentum then equation 8 can be written as:

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

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2 p^2\psi}{h^2} = 0 \quad \ldots\ldots 9$$

In chemistry it is important to express the Schrödinger equation in form of the energy as in equation 8 instead of in form of the linear momentum as in equation 9. Hence, if the system is a conservative i.e., the total energy is being constant respect to time where:

$$E = T + V = \frac{mv^2}{2} + V = \frac{p^2}{2m} + V \rightarrow$$

$$p^2 = 2m(E - V) \quad \ldots\ldots 10$$

Substitution equation 10 in equation 9:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m(E-V)\psi}{h^2} = 0 \quad \ldots\ldots 11$$

Rearranging of equation 11 is yielded:

$$\left(\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V\right)\psi = E\psi \quad \ldots\ldots 12$$

The limit $\frac{-h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V$ can be expressed by the Hamilton's operator $\hat{\mathcal{H}}$ then equation 12 can be written as:

$$\hat{\mathcal{H}}\psi = E\psi \quad \ldots\ldots 13$$

As shown from equation 13 it represent the Eigen value where ψ refers to the atomic and molecular orbitals in chemistry and E represents the energy of the electron. Equation 13 is the Schrödinger equation for the stable state i.e., the state that the energy of the particle is constant respect to the time. The above equation is derived according to the experimental facts by using the wave property of the matter but, the particle is moved through three dimension therefore; equation 13 can be written as:

$$\frac{-h^2}{8\pi^2 m}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] + V\psi = E\psi \quad \ldots\ldots 14$$

The interpretation of the function ψ:

As the system that selected in last to derive the Schrödinger equation has the dual properties i.e., the wave and the particle and ψ is the wave function. Max Born interpreted that the physical meaning of ψ which represents the electron where, he said that ψ can give the an idea for the probability density of the certain electron but ψ not represent the probability density of the certain electron because the probability it lies between zero and one (positive) where, zero and one refer to improbability and probability density of the certain electron respectively and ψ can be a negative as in Figure 1 above (sine wave) or can be as complex function ψ^*. In other words ψ can't expressed on the probability density of the electron but ψ^2 is the represent expression on the probability above if ψ is a real function. Generally, the probability is represented by $\psi\psi^*$ if ψ is complex function thus, in order to expression on the probability density of the particular electron in small volume dxdydz the exact expression is $\psi\psi^*$dxdydz. Hence, the wave function represent the state of the particle and the physical interpretation for this function represented by the probability density of the particular particle in special position in a space therefore; the wave function should be physically accepted.

Quantum Mechanics Postulates:

Postulate I.: For any possible state of a system, there is a function ψ, of the coordinates of the parts of the system and time that completely describes the system. For a single particle described by Cartesian coordinates, we can write:

$$\Psi = \Psi(x, y, z, t) \quad \text{......1}$$

For two particles, the coordinates of each particle must be specified so that

$$\Psi = \Psi(x_1, y_1, z_1, x_2, y_2, z_2, t) \quad \text{......2}$$

For a general system, we can use generalized coordinates, q_i

$$\Psi = \Psi(q_i,\ t) \quad \text{......3}$$

Since the model is that of a wave ψ is called a *wave function*. The state of the system that i describes is called the *quantum state*. The wave function squared, ψ^2 is proportional to probability. Since ψ may be complex, we are interested in $\psi\ \psi^*$ where ψ^* is the ***complex conjugate*** of ψ. The complex conjugate is the same function with i replaced by −i, where $i = \sqrt{-1}$. For example, if we square the function (x + ib) we obtain:

$$(x + ib)(x + ib) = x^2 + 2ibx + i^2b^2 = x^2 + 2ibx - b^2 \quad \text{......4}$$

And the resulting function is still complex. If we multiply (x + ib) by its complex conjugate (x − ib), we obtain:

$$(x + ib)(x - ib) = x^2 + ibx - ibx - i^2b^2 = x^2 + b^2 \quad \text{......5}$$

Which is a real function.

The quantity $\psi\ \psi^*\ d\tau$ is proportional to the probability of finding the particles of the system in the volume element, $d\tau = dx\ dy\ dz$. We require that the total probability be unity (1) so that the particle must be *somewhere*. That is:

$$\int_0^{all\ space} \Psi\Psi^* d\tau = 1 \quad \text{......6}$$

Single valued and *continuous*. These conditions describe a "well-behaved" wave function. The reasons for these requirements are as follows: الشروط التي تصف السلوك الممتاز للدالة الموجية

1. **Finite:** A probability of unity (1.00) denotes a "sure thing." A probability of (0) means that a certain event cannot happen. Therefore, probability varies from 0 to unity. If ψ were infinite, the probability could be greater than 1.
2. **Single Valued:** In a given region of space, there is only one probability of finding a particle. Similarly, in a hydrogen atom, there is a single probability of finding the electron at some specified distance from the nucleus. There are not two different probabilities of finding the electron at some given distance from the nucleus.
3. **Continuous:** If there is a certain probability of finding an electron at a given distance from the nucleus in a hydrogen atom, there will be a slightly different probability if the distance is changed slightly. The probability does not suddenly double if the distance is changed by 0.01%. The probability function does not have discontinuities so the wave function must be continuous. If two functions ϕ_1 and ϕ_2 have the property that:

$$\int \phi_1 \phi_2^* \, d\tau = 0 \ or \ \int \phi_1^* \phi_2 \, d\tau = 0 \quad \ldots\ldots 7$$

They are said to be *orthogonal*. Whether the integral vanishes may depend on the limits of integration, and hence one speaks of *orthogonality* within a certain interval. Therefore, the limits of integration must be clear. In the previous case, the integration is carried out over the possible range of the coordinates used in $d\tau$. If the coordinates are x, y, and z, the limits are from $-\infty$ to $+\infty$ for each variable. If the coordinates are r, θ, and ϕ, the limits of integration are 0 to ∞, 0 to π, and 0 to 2π, respectively.

Classical mechanics: ***The classical mechanics*** science studied the motion of the bodies and the forces that affected on them. It is prove that the using of mathematical science and its theories leads to discover and explain the natural effects (***phenomenon***) in the universal. ***The classical mechanics*** is used for the system that its contents are greater than atoms and molecules only. This science depends upon Newton's law of motion then the exceptions is treated by Joseph Lagrange and William Hamilton.

Because the classical mechanic not suitable for the atoms and molecules. Hence, ***quantum mechanics*** discovered to treat exactly this case. The presence of quantum mechanics initiated relative to classical mechanics hence, some of lows in classical mechanics are using (yet) in quantum mechanics therefore; classical mechanics should be studied briefly when the quantum mechanics is studied. is used

The principles of classical mechanics for solving the problems for the motion of bodies is studying the contents' motion in movement's bodies under different forces and the primarily conditions that surrounded by the motion. Thus, the differential equation for Newton's second law should be solved: حركة المحتويات داخل الاجسام المتحركة

$v = \frac{ds}{dt}$, $a = \frac{dv}{dt} \leftrightarrow a = \frac{d^2s}{dt^2}$

$F = ma$ ....48 ازاحة shift

Where (F) is the applied force, (m) is the mass of the body and (a) is the ground gravity's acceleration. Q1 How you can prove that F=ma is a differential equation

Conservative System:

If the product of the sum of both kinetic and potential is a constant for the particular system with respect to the time, the system is called *conservative system*. Whereas: Q what do you mean by isolated system?

$T + V = E$ 49

Where (T) is the kinetic energy, (V) is the potential energy and (E) is the total energy. Conservative system is an isolated system which is not affected by the external force. On the other hand if any property for any mechanical system is independent on the time the property then is called ***"the constant of motion for the system"***. Thus, E in equation 49 is the constant of motion for the system. answer adiabatic system

independent of time but T+V are dependent of time

$F(x) = m\frac{d^2x}{dt^2}$..50

$F(i) = -\nabla V$..51

For the kinetic Hamilton's equations of this system, the momentum is calculated according to the equations 71 & 84:

generalized momentum

$$p_x = \frac{\partial L}{\partial \dot{x}} = (m_1 + m_2)\dot{X} \quad \text{.......89}$$

generalized coordinate

$$p_y = (m_1 + m_2)\dot{Y} \quad \text{.......90}$$

$$p_z = (m_1 + m_2)\dot{Z} \quad \text{.......91}$$

Since, the Hamilton's function can be written according to the equation 72 as in the following:

$$\mathcal{H} = \frac{1}{2(m_1+m_2)}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z) \quad \text{.......92}$$

Then Hamilton's equations according to equation 70 are:

$$\frac{\partial \mathcal{H}}{\partial q_j} = \frac{-\partial L}{\partial q_j} = -\dot{p}_j \quad \text{.......70}$$

Linear momentum

$$\dot{p}_x = -\frac{\partial \mathcal{H}}{\partial x} = 0, \dot{p}_y = 0, \dot{p}_z = 0 \quad \text{.......93}$$

The last equations (93) are same as in Lagrange's' equations.

The last the classical mechanics assumed that:

1. The case of any system can be described at any time experimentally (in laboratory) by measuring the place and the vectorial velocity exactly for all system's constituents. i.e., it can be deduced (verify) the movements of the particle in the certain system.
2. The verifying of the mobile of the particular particle for any system means that the energy and the momentum of any particle at any time. Can be determined

The above two postulates result the following:

1. The exact determination of the dynamics variables that varied at same time in classical system depends only upon the errors in the devices that used for the measurements of these variables.
2. The measured dynamics variables at same time cannot be determined

Homework:

1. Write the Hamilton's equation for Li atoms by graphical plotting.
2. Derived equations 69& 70.
3. Prove that Hamilton's function is equal the total energy for the particular system.

This equation predicted the observed relationship between the frequencies of radiation emitted and the intensity. The successful interpretation of blackbody radiation by Planck provided the basis for considering energy as being quantized, which is so fundamental to our understanding of atomic and molecular structure and our experimental methods for studying matter. Also, we now have the relationship between the frequency of radiation and its energy,

$E = h\upsilon$ 7

These ideas will be seen many times as one studies quantum mechanics and its application to physical problems.

The Line Spectrum of Atomic Hydrogen:

When gaseous hydrogen is enclosed in a glass tube in such a way that a high potential difference can be placed across the tube, the gas emits a brilliant reddish-purple light. If this light is viewed through a spectroscope, the four major lines in the visible *line spectrum* of hydrogen are seen. There are other lines that occur in other regions of the electromagnetic spectrum that are not visible to the eye. In this visible part of the hydrogen emission spectrum, the lines have the wavelengths

$H_\alpha = 6562.8 A^\circ = \boxed{656.28\ nm}$ (red), $H_\beta = 4961.3\ A^\circ = \boxed{496.13\ nm}$ (green)

$H_\gamma = 4340.5\ A^\circ = \boxed{434.05}$ nm (blue), $H_\delta = 4101.7\ A^\circ = \boxed{410.17}$ nm (violet).

As shown in Figure 2, electromagnetic radiation is alternating electric and magnetic fields that are perpendicular and in phase. Planck showed that the energy of the electromagnetic radiation is proportional to the frequency, v, so that

$E = h\upsilon$ 7

Since electromagnetic radiation is a transverse wave, there is a relationship between the wavelength, λ and the frequency, v. Frequency is expressed in terms of cycles per unit time, but a "cycle" is simply a count, which carries no units. Therefore, the dimensions of frequency are "cycles"/time or 1/time.

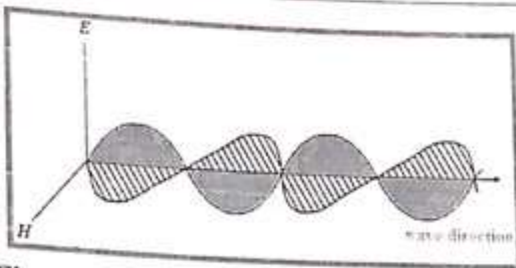

Figure 2: Electromagnetic radiation.

The wavelength is a distance so its dimension is distance (or length). The product of wavelength and frequency is

$$\lambda\nu = distance \times \frac{1}{time} = \frac{distance}{time} = velocity = V \qquad \text{......8}$$

In the case of electromagnetic radiation, the velocity of light is c, which is 3.00×10^{10} cm/s. Therefore, $\lambda\nu = c$ and

$$E = h\nu = \frac{hc}{\lambda} \qquad \text{......9}$$

In 1885, Balmer discovered an empirical formula that would predict the preceding wavelengths. Neither Balmer nor anyone else knew why this formula worked, but it did predict the wavelengths of the lines accurately. Balmer's formula is:

$$\lambda(cm) = 3645.6 \times 10^{-8}\left(\frac{n^2}{n^2-2^2}\right) \Rightarrow \frac{1}{\lambda} = \frac{1}{3645.6\times10^{-8}} \times \left(\frac{n^2-2^2}{n^2}\right) \qquad \text{......10}$$

The constant 3645.6×10^{-8} has units of centimeters and n represents a whole number larger than 2. Using this formula, Balmer was able to predict the existence of a $\boxed{\text{fifth line}}$. This line was discovered to exist at the boundary between the visible and the ultraviolet regions of the spectrum. The measured wavelength of this line agreed almost perfectly with Balmer's prediction. Balmer's empirical formula also predicted the existence of other lines in the infrared (IR) and ultraviolet (UV) regions of the spectrum of hydrogen. These are as follows:

Lyman series: $n^2/(n^2-1^2)$, where n = 2, 3,... (1906–1914, UV)

Paschen series: $n^2/(n^2-3^2)$, where n = 4, 5,...(1908, IR)

Brackett series: $n^2/(n^2-4^2)$, where n = 5, 6,...(1922, IR) → Far

Pfund series: $n^2/(n^2-5^2)$, where n = 6, 7,...(1924, IR). → Far

Balmer's formula can be written in terms of 1/wavelength and is usually seen in this form. The equation becomes

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad \text{.......... 11}$$

Where R is a constant known as the *Rydberg constant*, 109,677.76 cm^{-1}. The quantity $1/\lambda$ is called the *wave number* and is expressed in units of The empirical formulas can be combined into a general form:

$$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad n_1 < n_2 \quad \text{.......... 12}$$

When n_1=1 and n_2= 2, 3, 4... The Lyman series is predicted. For = 2, 3, 4,..... the Balmer series is predicted, and so on. Other empirical formulas that correlated lines in the spectra of other atoms were found, but the same constant R occurred in these formulas. At the time, no one was able to relate these formulas to classical electromagnetic theory.

The Bohr Model for the Hydrogen Atom

It is not surprising that the spectrum of the hydrogen atom was the first to be explained since it is the simplest atom. E. Rutherford had shown in 1911 that the model of the atom is one in which a small but massive positive region is located in the center of the atom and the negative region surrounds it. Applying this model to the hydrogen atom, the single proton is located as the nucleus while a single electron surrounds or moves around it. N. Bohr incorporated these ideas into the first dynamic model of the hydrogen atom in 1913, supposing the electron to be governed by the laws of classical or Newtonian physics. There were problems, however, that could not be answered by the laws of classical mechanics. For example, it had been shown that an accelerated electric charge radiates electromagnetic energy (as does an antenna for the emission of radio frequency waves). To account for the fact that an atom is a stable entity, it was observed that the electron must move around the nucleus in such a way that the centrifugal force exactly balances the electrostatic force of attraction between the proton and the electron. Since the electron is moving in some kind of circular orbit, it must constantly undergo acceleration and should radiate electromagnetic energy by the laws of classical physics. Because the Balmer series of lines in the spectrum of atomic hydrogen had been observed earlier, physicists attempted to use the laws of classical physics to explain a structure of the hydrogen atom that would give rise to these lines. It was recognized from Rutherford's work that the nucleus of an atom was surrounded by the electrons and that the electrons must be moving. In fact, no system of electric charges can be in equilibrium at rest. While the electron in the hydrogen atom must be moving, there is a major problem. If the electron circles the nucleus, it is undergoing a constant change in direction as shown in Figure 3.

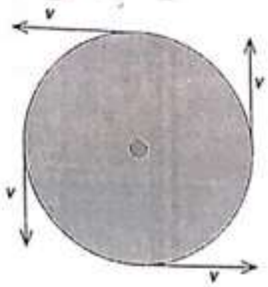

Figure 3: The change in velocity vector for circular motion.

Velocity has both a magnitude and a direction. Changing direction constitutes a change in velocity, and the change in velocity with time is acceleration. The laws of classical electromagnetic theory predict that an accelerated electric charge should radiate electromagnetic energy. If the electron did emit electromagnetic energy, it would lose part of its energy, and as it did so it would spiral into the nucleus and the atom would collapse. Also, electromagnetic energy of a *continuous* nature would be emitted, not just a few lines. Bohr had to assume that there were certain orbits (the "allowed orbits") in which the electron could move without radiating electromagnetic energy. These orbits were characterized by the relationship:

$$mvr = n\frac{h}{2\pi} \quad \text{.......... 13}$$

Where m is the mass of the electron, v is its velocity, r is the radius of the orbit, h is Planck's constant, and n is an integer, 1, 2, 3, ... Since n is a whole number, it is called a *quantum number*. This enabled the problem to be solved, but no one knew why this worked. Bohr also assumed that the emitted spectral lines resulted from the electron falling from an orbital of higher n to one of lower n.

$= -\frac{mv^2}{r}$

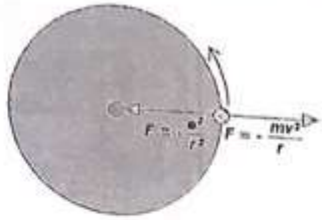

Figure 4: The forces on the electron in circular motion in a hydrogen atom.

القوى المؤثرة على المدار الالكتروني يجب ان تكون مقدارها مساوي للـ

Figure 4 shows the forces acting on the orbiting electron. The magnitudes of these forces must be equal for an electron to be e in a stable orbit, so if e is the electron charge,

$$\frac{mv^2}{r} = \frac{e^2}{r^2} \quad \text{.......} \text{القوة المؤثرة} \text{.......} 14$$

Therefore, solving this equation for v gives:

$$v = \sqrt{\frac{e^2}{mr}} \quad \text{.......} 15$$

$mvr = \frac{nh}{2\pi}$ مما نعوض في معادلة

From the Bohr assumption that

$$\sqrt{\frac{e^2}{mr}} = \frac{nh}{2\pi mr} \quad \text{.......} 16$$

Solving for r we obtain

$$r = \frac{n^2h^2}{4\pi^2me^2} \quad \text{.......} 17$$

This relationship shows that the radii of the allowed orbits increase as n^2, h, m, and e are constants). Therefore, the orbit with n = 2 is four times as large as that with n = 1; the orbit with n = 3 is nine times as large as that with n = 1, etc. Figure 5 shows the first few allowed orbits drawn to scale.

Figure 5: The first four orbits in the hydrogen atom drawn to scale.

The units on r can be found from the units on the constants since e is measured in *electrostatic units* (esu) and an esu is in $g^{1/2}$ $cm^{3/2}$ s^{-1} Therefore,

$$\frac{[(g.cm^2/s^2)s]^2}{g\left(g^{\frac{1}{2}}cm^{\frac{3}{2}}/s\right)^2} = cm \quad \text{......18}$$

Home Work (2)

The total energy is the sum of the electrostatic energy (potential) and the kinetic energy of the moving electron (total energy = kinetic + potential):

$$E = \frac{1}{2}mv^2 - \frac{e^2}{r} \quad \text{......19}$$

From equating the magnitudes of the centripetal and centrifugal forces, we know that

1 Static Coulomb = 3.34×10^{-10} C

$$\frac{mv^2}{r} = \frac{e^2}{r^2} \quad \text{......20}$$

1 Static Coulomb = $dyne^{1/2}$ cm

1 eV = 1.6

Or:

$$mv^2 = \frac{e^2}{r} \quad \text{......21}$$

Multiplying both sides of this equation by 1/2 gives:

1 esu = 3.

$$\frac{1}{2}mv^2 = \frac{e^2}{2r} \quad \text{......22}$$

The left-hand side of Eq. 22 is simply the kinetic energy of the electron, and substituting this into Eq. 19 yields:

$$E = \frac{e^2}{2r} - \frac{e^2}{r} = -\frac{e^2}{2r} \quad \text{......23}$$

We found earlier in Eq.17 that:

$$r = \frac{n^2h^2}{4\pi^2me^2} \quad \text{......17}$$

And when we substitute this result for r in Eq. 23 we obtain

1 N = 10^5 dyne

$$E = -\frac{e^2}{2r} = \frac{-e^2}{2\left(\frac{n^2h^2}{4\pi^2me^2}\right)} \quad \text{......24}$$

From this equation, we see that the energy of the electron in the allowed orbits varies inversely as n^2. Note also that the energy is negative and becomes less negative as n increases. At n =∞ (complete separation of the proton and electron), E = 0 and there is no binding energy of the electron to the nucleus. The units for E in the previous equation depend on the units used for the constants. If the is in ergs seconds, the mass of the electron is in grams, and the charge on the electron, e, is in esu, we have

$$E = \frac{g\left(g^{\frac{1}{2}}cm^{\frac{3}{2}}/s\right)^4}{[(g.cm^2/s^2)s]^2} = \frac{g.cm^2}{s^2} = erg \quad \ldots\ldots 25$$

We can then use conversion factors to obtain the energy in any other desired units. If we write the expression for energy in the form

$$E = -\frac{2\pi^2 me^4}{n^2h^2} \quad \ldots\ldots 26$$

We can evaluate the collection of constants when n = 1 to give -2.17×10^{-11} erg and assign various values for n to evaluate the energies of the allowed orbits:

n = 1, E = -21.7×10^{-12} erg, n = 2, E = -5.43×10^{-12} erg, n = 3, E = -2.41×10^{-12} erg, n = 4, E = -1.36×10^{-12} erg, n = 5, E = -0.87×10^{-12} erg, n = 6, E = -0.63×10^{-12} erg, n = ∞, E = 0.

Figure 6 shows an energy level diagram in which the energies are shown graphically to scale for these values of n.

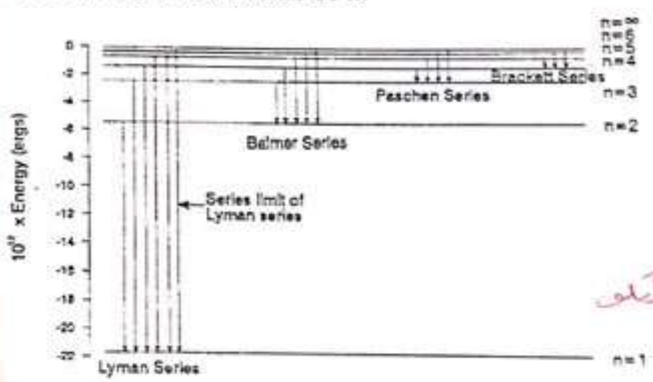

Figure 6: Energy level diagram for the hydrogen atom.

Note that the energy levels get closer together (converge) as the n value increases. Causing the electron to be moved to a higher energy level requires energy because the positive and negative charges are held together by a strong electrostatic force. Complete removal of the electron requires an amount of energy known as the *ionization potential* (or ionization energy) and corresponds to moving the electron to the orbital where n = ∞. The electron in the lowest energy state is held with an energy of -21.7×10^{-12} erg, and at n = ∞ the energy is 0. Therefore, the ionization potential for the H atom is 21.7×10^{-12} erg. If we consider the energy difference between the n = 2 and the n = 3 orbits, we see that the difference is 3.02×10^{-12} erg. Calculating the wavelength of light having this energy, we find:

$E = h\upsilon = \frac{hc}{\lambda}$ 9

Or:

$$\lambda = \frac{hc}{E} = \frac{6.63\times10^{-27}\,erg.s\times3\times10^{10}\,cm.s^{-1}}{3.02\times10^{-12}\,erg} = 6.59 \times 10^{-5}\,cm.$$

Which matches the wavelength of one of the lines in the Balmer series! Using the energy difference between the n = 2 and the n = 4 orbits leads to a wavelength of 4.89×10^{-5} cm, which matches the wavelength of another line in Balmer's series. Finally, the energy difference between the n = 2 and the n =∞ orbits leads to a wavelength of 3.66×10^{-5}cm, and this is the wavelength of the ***series limit*** of the Balmer series. It should be readily apparent that Balmer's series corresponds to light emitted as the electron falls from states with n = 3, 4, 5, ..., ∞, to the orbit with n = 2. We could calculate the energies of lines emitted as the electron falls from orbits with n = 2, 3, ... , ∞, to the orbital with n = 1 and find that these energies match the lines in another observed spectral series, the ***Lyman*** series. In that case, the wavelengths of the spectral lines are so short that the lines are no longer in the visible region of the spectrum, but rather they are in the ultraviolet region. Other series of lines correspond to the transitions from higher n values to n = 3 (Paschen series, infrared), n = 4 (Brackett series, infrared), and n = 5 (Pfund series, far infrared) as the lower values. The fact that the series limit for the Lyman series represents the quantity of energy that would be required to remove the electron suggests that this is one way to obtain the ionization potential for hydrogen. Note that energy is released (negative sign) when the electron falls from the orbital with n =∞ to the one with n = 1 and that energy is absorbed (positive sign) when the electron is excited from the orbital with n = 1 to the one corresponding to n =∞. Ionization energies are the energies required to remove electrons from atoms, and they are always positive.

The Photoelectric Effect

In 1887, ***H.R.Hertz*** observed that the gap between metal electrodes became a better conductor when ultraviolet light was shined on the apparatus. Soon after, W.Hallwachs observed that a negatively charged zinc surface lost its negative charge when ultraviolet light was shined on it. The negative charges that were lost were identified to be electrons from their behavior in a magnetic field. The phenomenon of an electric current