Hydrogen atom Correct Structure

* Spectroscopy

Branch of the ~~Spectroscopy~~ physics which deals with the observation and interpretation of the radiation emitted and absorbed by the atoms and molecules. And through the light on their structure. It provides information not only about the arrangement and motion of the outer electron but also information about the angular momentum, magnetic moment, charge distribution and magnetism of the Nucleous (Study of the hyperfine structure, nuclear magnetic resonance etc.)

~~It was~~ It Sir Isaac Newton who originated spectroscopy by showing that a prism reflects blue light more than red ~~light~~, thus ~~shows~~ forming a band ~~Structure~~ of colours known as a spectrum.

In 1980's Fraunhofer used a photograph to measure the wavelength of lines that had not been before, in light from the sun and he deduced the existence of new element called the He

In 1988, the Swidish Professor, J. Rydberg found the spectral lines in the hydrogen atom obey the following mathematical formula:

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right]$$

where n & n' are whole ~~numbers~~

by chang the role of n & n' a a series of lines are determined by name as Balmer series, lymen's ~~D~~ series etc.

To describe such series of lines it is convenient to define the reciprocal of the transition wavelength as the wave number $\bar{\nu}$ (cm^{-1})

$$\bar{\nu} = \frac{1}{\lambda}.$$

wave numbers are very useful in atomic physics since they easily evaluated from measured wavelengths without any conversion factor.

in 1913, Bohr put forward a ~~so~~ radical new model of the hydrogen atom using quantum mechanics.

At the same time as Bohr was working on his model of the hydrogen atom, H. G. J. Moseley measured the X-ray spectra of many elements. He established that

$$\sqrt{f} \propto Z$$

The development of the ideas of atomic structure was linked to experiments on the emission, and absorption of radiation from the atoms. The emission of radiation was considered as something that just ~~too~~ has to happen in order to carry away the energy when an electron jumps from one allowed orbit to another. But the mechanism was not explained. It was the Einstein, who explained the emission and absorption of the radiation of the atom by the ~~cofficient~~ coefficients, called Einstein cofficient (A_{21} & B_{12}).

In 1986, Zeeman ~~stud~~ ~~studies the~~ worked on the effect of a magnetic field on atoms. This observation is called the Zeeman effect.

Schrodinger's Time-independent Equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0 \quad (1)$$

Solution of Schrodinger Equation for Coulomb field (Quantum mechanical Treatment of one-electron atom).

Schrodinger equation for one-electron atom like hydrogen atom. It consists of positively charged nucleus $(+Ze)$ and negatively charged electron $(-e)$.

In one electron system, the mass of the electron is m & the mass of the nucleus $= M$. Now may replace the mass of the system (electron + nucleus) by μ (reduced mass)

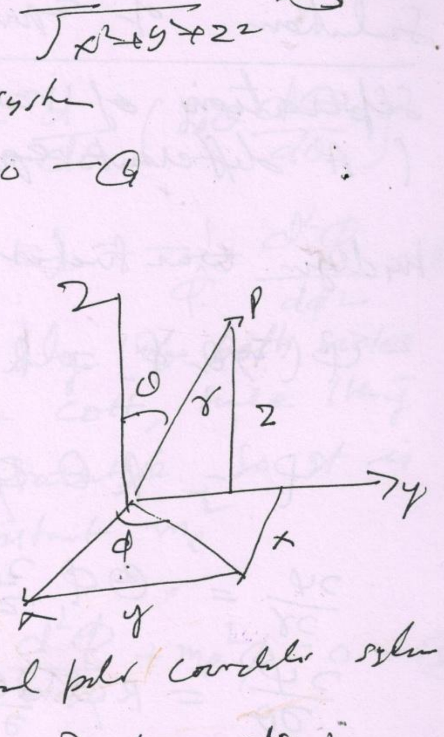
$$\mu = \frac{Mm}{m+M} \quad \text{---(2)}$$

Potential energy $V(x,y,z) = -\dfrac{Ze^2}{\sqrt{x^2+y^2+z^2}}$ ---(3).

The schrodinger equation for such system

$$\nabla^2\psi + \frac{2\mu}{\hbar^2}(E-V)\psi = 0 \quad \text{---(4)}$$

$$x = r\sin\theta\cos\phi \quad \text{---(5)}$$
$$y = r\sin\theta\sin\phi \quad \text{---(6)}$$
$$z = r\cos\theta \quad \text{---(7)}$$



where $r = \sqrt{x^2+y^2+z^2}$ ---(8)

$$\theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right) \quad \text{---(8)}$$

$$\phi = \tan^{-1}(y/x) \quad \text{---(10)}$$

The schrodinger equation in spherical polar coordinate system

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}(E-V)\psi = 0 \quad \text{---(11)}$$

~~Separation of variables~~

~~The advantage of writing~~

Potential energy can be written as in the H_2 atom

$$V = V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

Hence equation (11) can be written as (by multiplying $r^2\sin^2\theta$)

$$\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu r^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) = 0 \quad (12)$$

Solution of Equation (12)

Separation of variables
(A different equation for each variable)

Hydrogen wave function

$$\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi) \quad (13)$$

$$\psi = R\Theta\Phi \quad (14)$$

$$\frac{\partial\psi}{\partial r} = \Theta\Phi\frac{\partial R}{\partial r} \quad (15)$$

$$\frac{\partial\psi}{\partial\theta} = R\Phi\frac{\partial\Theta}{\partial\theta} \quad (16)$$

$$\frac{\partial^2\psi}{\partial\phi^2} = R\Theta\frac{\partial^2\Phi}{\partial\phi^2} \quad (17)$$

Substituting (14) (15) (16) & (17) in (12) and divide by $R\Theta\Phi$, we get

$$\underbrace{\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)}_{(I)} + \underbrace{\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)}_{(II)}$$

$$+ \underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}_{(III)} + \underbrace{\frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right)\sin^2\theta}_{(IV)} = 0 \quad \text{--- (18)}$$

Third term in (18) is a function of azimuthal angle ϕ only, whereas the other terms are function of r & θ only. Now rearranging the (18),

$$\Rightarrow \frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

$$+ \frac{2\mu r^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} \quad \text{--- (19)}$$

This equation can be correct only if both sides of it are equal to the same const, since they are function of different variable. So it is convenient to call this constant m_l^2

$$\Rightarrow -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m_l^2 \Rightarrow \frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0 \quad \text{--- (20)}$$

Equation (19) becomes as

(20)

$$\cancel{\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin^2\theta}{}}$$

$$\frac{1}{R}\cdot\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)$$
$$=\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - (21)$$

Again in Eqtn (21) appears differt variable both sides. It requires the same constant on both sides, say $l(l+1)$

$$\Rightarrow \frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)=l(l+1) \quad (22)$$

&

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)=l(l+1) \quad (23)$$

∴ Equtns (20), (22) & (23) can be written as

$$\frac{d^2\Phi}{d\phi^2}+m_l^2\Phi=0 \longrightarrow (24)$$

[Equation for Φ]

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]\Theta=0 \quad (25)$$

[Eqtn for Θ]

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)-\frac{l(l+1)}{r^2}\right]R=0 \quad (26)$$

[Equation for R]

Solution of ϕ- Equation

$$\frac{d^2\phi}{d\phi^2} + m_l^2\phi = 0$$

Its solution is given by

$$\phi(\phi) = A e^{i m_l \phi} \quad —(27)$$

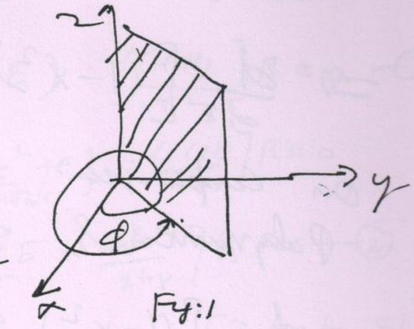


Fig: 1

From Fig. 1 it is clear that ϕ & $\phi + 2\pi$ both identically same. Hence it must be true that $\phi(\phi) = \phi(\phi + 2\pi)$

$$\Rightarrow A e^{i m_l \phi} = A e^{i m_l(\phi + 2\pi)}$$

$$\Rightarrow 1 = e^{i m_l \times 2\pi}$$

$$\Rightarrow m_l = 0, \pm 1, \pm 2, \pm 3, \ldots$$

where $m_l \rightarrow$ magnetic quantum number
(m)

$l \rightarrow$ orbital quantum number

Solution of Θ Equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta} \right]\Theta = 0$$

Let $l(l+1) = \lambda$, $m_l = m$.

and putting $x = \cos\theta$

$$\frac{d\Theta}{d\theta} = \frac{dx}{d\theta}\frac{d\Theta}{dx} = -\sin\theta \frac{d\Theta}{dx} \quad —(28)$$

$$\Rightarrow \frac{d}{d\theta} = -\sin\theta \frac{d}{dx}$$

$$\sin\theta \frac{d\Theta}{d\theta} = -\sin^2\theta \frac{d\Theta}{dx}.$$

$$\Rightarrow \sin\theta \frac{d\Theta}{d\theta} = -(1-x^2)\frac{d\Theta}{dx} \quad —(29)$$

Putting equation (28) & (29) in Θ equation (P-)

$$\Rightarrow \frac{d}{dx}\left\{(1-x^2)\frac{d\Theta}{dx}\right\} + \left(\lambda - \frac{m^2}{1-x^2}\right)\Theta = 0$$

$$\Rightarrow \frac{d}{dx}\left[(1-x^2)\frac{d\Theta}{dx}\right] + \left[l(l+1) - \frac{m^2}{1-x^2}\right]\Theta = 0 \quad -(30)$$

On comparison of (30) with Legendre Polynomials equation

$$\frac{d}{dx}\left[(1-x^2)\frac{d}{dx}P_l^m(x)\right] + \left[l(l+1) - \frac{m^2}{1-x^2}\right]P_l^m(x) = 0 \quad -(31)$$

gives

$$\Theta = B\, P_l^m(x) \quad -(32)$$

$$\Theta_{l,m}(\theta) = B\, P_l^m(\cos\theta) \quad -(32)$$

where B → normalized ~~wave factor~~ constant.

$$B = \sqrt{\left[\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right]}$$

Thus the solution is

$$\Theta_{l,m}(\theta) = \sqrt{\left[\frac{(2l+1)}{2}\frac{(l-m)!}{(l+m)!}\right]}\, P_l^m(\cos\theta) \quad -(33)$$

with $P_l^m(x) = (1-x^2)^{m/2}\dfrac{d^m}{dx^m}P_l(x)$, $-(34)$

and $P_l(x) = \dfrac{1}{2^l\, l!}\left(\dfrac{d}{dx}\right)^l (x^2-1)^l$. $-(35)$

where $x = \cos\theta$ $-(36)$

Solution of R-Equation

The radial R-equation is given by as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)-\frac{l(l+1)}{r^2}\right]R=0 \quad (1)$$

$$\Rightarrow \frac{1}{r^2}\left(r^2\frac{\partial^2 R}{\partial r^2}\right)+\frac{1}{r^2}2r\cdot\frac{\partial R}{\partial r}+\left[\frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)-\frac{l(l+1)}{r^2}\right]R=0$$

$$\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}+\left[-\frac{l(l+1)}{r^2}+\frac{2\mu}{\hbar^2}E+\frac{2\mu k e^2}{\hbar^2 r}\right]R=0 \quad (2)$$

$$\left[\text{Taking } \frac{1}{4\pi\epsilon_0}=1\right]$$

According to the classical mechanics
if $E<0$, bound state
$E>0$ unbound state

Let us consider the electron is in bound state of the H_2 atom. i.e. $E<0$, then let us substitute

$$\left.\begin{aligned} \alpha^2 &= -\frac{2\mu E}{\hbar^2}, \\ \lambda &= \frac{\mu k e^2}{\hbar^2\alpha} \end{aligned}\right] \quad (3)$$

putting Eqn (3) into Equation no. (2), then

$$\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}+\left[-\frac{l(l+1)}{r^2}-\alpha^2+\frac{2\lambda\alpha}{r}\right]R=0 \quad (4)$$

Let ρ be an independent variable such that,

$$\left.\begin{aligned} \rho &= 2\alpha r \\ \frac{\partial\rho}{\partial r} &= 2\alpha \end{aligned}\right] \quad (5)$$

So that we have that

$$\frac{\partial R}{\partial r}=\frac{\partial R}{\partial\rho}\cdot\frac{\partial\rho}{\partial r}=(2\alpha)\frac{\partial R}{\partial\rho} \quad (6)$$

$$\frac{\partial^2 R}{\partial r^2}=(2\alpha)\frac{\partial}{\partial r}\left(\frac{\partial R}{\partial\rho}\right)=(2\alpha)\frac{\partial}{\partial r}\left(\frac{\partial R}{\partial\rho}\cdot\frac{\partial\rho}{\partial r}\right)$$

$$=(2\alpha)\left(\frac{\partial}{\partial r}\left(\frac{\partial R}{\partial\rho}\cdot(2\alpha)\right)\right)$$

$$\frac{\partial^2 R}{\partial r^2}=(4\alpha^2)\frac{\partial^2 R}{\partial\rho^2} \quad (7)$$

putting the value of Equation (6) & (7) into Equation (4)

P-

$$4\alpha^2 \frac{\partial^2 R}{\partial \rho^2} + \frac{2}{r}(2\alpha)\frac{\partial R}{\partial \rho} + \left[-\frac{l(l+1)}{r^2} - \alpha^2 + \frac{2\lambda\alpha}{r}\right]R =$$

Dividing both sides by $4\alpha^2$, we get

$$\Rightarrow \frac{\partial^2 R}{\partial \rho^2} + \frac{1}{r\alpha}\frac{\partial R}{\partial \rho} + \left[-\frac{l(l+1)}{4\alpha^2 r^2} - \frac{1}{4} + \frac{\lambda}{2\alpha r}\right]R = 0$$

$$\Rightarrow \frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} + \left[-\frac{l(l+1)}{\rho^2} - \frac{1}{4} + \frac{\lambda}{\rho}\right]R = 0 \quad \text{— (8)}$$

Asymtotic Behaviour

if $\rho \to \infty$, then Equation (8) becomes

$$\frac{\partial^2 R(\rho)}{\partial \rho^2} - \frac{1}{4} R(\rho) = 0 \quad \text{— (9)}$$

Solution of Equation (9) is

$$\left.\begin{aligned} R(\rho) &= F(\rho)e^{+\rho/2} \quad \text{OR} \\ R(\rho) &= F(\rho)e^{-\rho/2} \end{aligned}\right] \to (10)$$

as ρ varies from 0 to ∞, then $\rho^{+\rho/2}$ goes to infinity, which not ~~an~~ acceptable wave function.

as ρ varies from 0 to ∞ then $e^{-\rho/2}$ goes to zero. i.e. acceptable wave function.

Therefore, the asymtotic solution of (8) will be

$$R(\rho) = F(\rho)\, e^{-\rho/2} \quad \text{—— (11)}$$

where $F(\rho)$ is another function of ρ.

putting Equation no. (11) in (8), then we get

$$\rho^2 \frac{\partial^2 F}{\partial \rho^2} + \rho(2-\rho)\frac{\partial F}{\partial \rho} + \left[\rho\lambda - l(l+1) - \rho\right]F = 0 \quad \text{— (12)}$$

if $\rho = 0$, then we get $-l(l+1)\,F(0) = 0$ or $F(0) = 0$; $l \neq 0$.

Therefore, we try a power series solution method for $F(\rho)$; it must not contain a constant term.

Hence. $$F(\rho) = \sum_{K=0}^{\infty} a_K \rho^{c+K} \quad \text{—— (13)}$$

putting Equation (13) into Equation (12), ~~we get~~

$$\sum_K a_K (\lambda - 1 - c - K)\rho^{c+K+1} + \sum_K a_K(c^2 + 2cK + K^2 + c + K - \ell^2 - \ell)\rho^{c+K} = 0 \quad \text{—— (15)}$$

Equation (15) is valid for all values of ρ only if the coefficient of each power of ρ vanishes separately. Equating the coefficient of ρ^c to zero, we have,

$$a_0(c^2 + 0 + 0 + c - \ell^2 - \ell) = 0$$

$a_0 \neq 0$, then

$$c^2 - c - \ell^2 - \ell = 0$$

$$(c - \ell) + (c^2 - \ell^2) \Rightarrow$$

$$(c - \ell)(c + \ell + 1) = 0 \Rightarrow c = \ell, \text{ or } c = -(\ell+1) \quad \text{—— (16)}$$

If $c = -(\ell+1)$, the 1st term in $F(\rho)$ will be $a_0 \rho^{-(\ell+1)}$

$$= a_0 \frac{\rho^{-\ell}}{\rho} \quad \text{—— (17)}$$

$F(\rho) \to \infty$ as $\rho \to 0$, then $F(\rho)$ is an acceptable function. Hence $c = \ell$ is the only acceptable value.

Setting the coefficient of $\rho^{\ell+K+1}$ in Eq. (15), we obtain

$$a_K(\lambda - 1 - \ell - K) + a_{K+1}(\cancel{\ell^2} + 2(\ell+1)K + K^2 + \ell + K - \cancel{\ell^2} - \ell) = 0$$

$$\Rightarrow a_{K+1} = \frac{\ell + K + 1 - \lambda}{(K+1)(K+2\ell+2)} a_K \quad \text{—— (18)}$$

This is called the recursion relation which allows us to

For the large of k, we get from (18),

$$\frac{a_{k+1}}{a_k} = \frac{1}{k} \quad \text{——} (19)$$

we know that

$$e^{\rho} = \sum_{k=0}^{\infty} \frac{1}{k!} \rho^k = \sum_{k=0}^{\infty} A_k \rho^k$$

$$\Rightarrow \frac{A_{k+1}}{A_k} = \frac{k!}{(k+1)!} = \frac{\cancel{k!}}{(k+1)\cancel{k!}} = \frac{1}{k+1} \to \frac{1}{k} \text{ as } k \to \infty$$

Therefore, as $k \to \infty$, the series for $F(\rho)$ behaves like $\rho^l e^{\rho}$ thus

$$R(\rho) = e^{-\rho/2} \rho^l e^{\rho} = \rho^l e^{\rho/2} \quad \text{——} (20)$$

as $\rho \to \infty$, the $R(\rho) \to \infty$ thus $R(\rho)$ is not acceptable. Therefore we have to break the series after a certain value of k, say n'. For this $a_{n'+1}$ must be zero.

i.e. $l + n' + 1 - \lambda = 0$ —— (21)

$\Rightarrow$ $n' = 0, 1, 2, 3 \ldots$

Energy Eigen values

Now Defining new quantum number n and given by

$$\underline{l + n' + 1} = \lambda$$

$$n = \lambda = \frac{Ke^2}{\hbar} \sqrt{\frac{\mu}{-2E}}$$

Squaring and simplifying

$$n^2 = \left(\frac{Ke^2}{\hbar}\right)^2 \frac{\mu}{-2E_n}$$

$$\Rightarrow E_n = -\frac{\mu e^4}{\ldots} = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} \quad n=1,$$

Since n' and l are integer including zero.

$$n = 1, 2, 3, \ldots$$

As $n \geq l+1$, highest value of l is $(n-1)$.

Therefore,

$$l = 0, 1, 2, 3, \ldots (n-1)$$

Here n is called the principle quantum no., which determines the energy.

~~But~~ The energy E_n is the same as obtained by the Bohr on the basis of quantum rules.

Radial wave function:

~~putting $\lambda = n$ in the~~

The ~~Equation (12) reduces as.~~

the Solution of (12) will be as

$$F(\rho) = \rho^l L(\rho) \longrightarrow (22), \text{ and } \lambda = n \quad -(23)$$

Therefore the equation (12) can be written as

$$\rho \frac{\partial^2 L(\rho)}{\partial \rho^2} + (2l+2-\rho)\frac{\partial L(\rho)}{\partial \rho} + (n-l-1)\, L(\rho) = 0 \quad -(24)$$

the Equation (24) is same as associated Laguerre polynomial of order p and degree $(q-p)$, denoted as $L_q^p(\rho)$.

Therefore (24) can be written as

$$\rho \frac{\partial^2 L_q^p}{\partial \rho^2} + (p+1-\rho)\frac{\partial L_q^p}{\partial \rho} + (q-p)\, L_q^p = 0 \quad -(25)$$

where $\left.\begin{array}{l} p = 2l+1 \\ \text{and} \\ n+l = q \end{array}\right] \quad -(26)$

The equation (23) (24) and (25) are identical, b

$$R_{n,l}(\rho) = F(\rho)\, e^{-\rho/2} = \cancel{N}\, e^{-\rho/2} \rho^{l} L^{2l+1}_{n+l}(\rho) \quad \text{—} (26)$$

Now using the condition of normalization

$$\int_0^\infty R^2_{nr}(r)\, r^2\, dr = 1 \quad \text{—} (27)$$

$\Rightarrow$ Here the factor $r^2 dr$ is necessary to convert the length dr in term of $\rho\, d\rho$. as

Since ~~$\rho = 2\lambda r = 2 \cdot \mu e^2$~~

$$r^2 dr = \frac{n^3 \hbar^6}{8\mu^3 k^3 e^6} \rho^2 d\rho \quad \text{—} (28)$$

Then eqn (26) become as

$$\frac{n^3 \hbar^6}{8\mu^3 K^3 e^6} |N|^2 \int_0^\infty \underline{e^{-\rho} \rho^{2l} \left(L^{2l+1}_{n+l}(\rho)\right)^2} \rho^2 dr = 1$$

$$= \frac{n^3 \hbar^6}{8\mu^3 k^3 e^6} (N)^2 \times \frac{2n[(n+l)!]^3}{(n-l-1)!} = 1$$

$$|N| = \pm \left[\left(\frac{2Z\mu k e^2}{n\hbar^2} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2} \quad \text{—} (29)$$

$$\text{then } R_{nl}(\rho) = -\left[\left(\frac{2Z}{n a_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2}$$

$$\times\, e^{-\rho/2} \rho^l L^{2l+1}_{n+l}(\rho) \quad \text{—} (30)$$

where $a_0 = \dfrac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$

Total wave function for H_2 atom is given by

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, \Theta_{ml}(\theta)\, \Phi_m(\phi) \quad \text{—} (31)$$

$$R_{nl}(r) = N_{nl}\, e^{-Zr/na_0} \left(\frac{2Zr}{na_0}\right)^{l} L^{2l+1}_{n+l}\left(\frac{2Zr}{na_0}\right) \quad (1)$$

where $N_{nl} \rightarrow$ const and

L^{2l+1}_{n+l} is associated Laguerre Polynomials

$$a_0 = \frac{h^2}{4\pi^2 \mu e^2}$$

~~These eigen values~~

Interpretation of Quantum Numbers

The three quantum number which arise in a natural way during search of acceptable solutions of the Schrodinger equation may be tabulated as

$n = 1, 2, 3, \ldots$

$l = 0, 1, 2, \ldots$

$m_l(m) = 0, \pm 1, \pm 2, \pm 3$

Interpretation of n

Schrodinger equation, the energy of one-electron atom in the bound state

$$E_n = -\frac{2\pi^2 \mu Z^2 e^4}{n^2 h^2} = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}, \quad n = 1, 2, 3, \ldots$$

This is the same as observed in the Bohr's model; n quantises the total energy of nth state of the atom. Hence n is called the total or principal quantum no.

Interpretation of l

we consider the radial wave equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{8\pi^2\mu}{h^2}(E-V(r))-\frac{l(l+1)}{r^2}\right]R=0 \quad -(1)$$

the total energy E of the atom consists of kinetic energy K and potential energy V of the electron. The K.E has two parts, K_{radial} → due to electron's motion towards or away from the Nucleus

and

$K_{orbital}$ → due to the motion around the nucleus.

Then $E = K_{radial} + K_{orbital} + V(r)$

putting this in Equation (1)

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{8\pi^2\mu}{h^2}\left[K_{radial}+K_{orbital}-\frac{h^2}{8\pi^2\mu}\left[\frac{l(l+1)}{r^2}\right]\right]\right]R=0 \quad -(2)$$

This radial Equation is concerned only with the radial motion of the electron. Hence it must be free from $K_{orbital}$. This is possible only when the last two terms cancelled out each other i.e

i.e. $K_{orbital} = \frac{h^2}{8\pi^2\mu}\left[\frac{l(l+1)}{r^2}\right] \quad -(3)$

$[\vec{L}]$ (angular momentum) $= \mu v r \quad -(4)$

$K_{orbital} = \frac{1}{2}\mu v^2 = \frac{\vec{L}^2}{2\mu r^2} \quad -(4)$

(4) = (5)

$$\frac{L^2}{2\mu r^2} = \frac{h^2}{8\pi^2\mu}\left(\frac{l(l+1)}{r^2}\right)$$

$$L^2 = l(l+1)\frac{h^2}{4\pi^2}$$

$$|L| = \sqrt{l(l+1)}\,\frac{h}{2\pi} \quad \text{— (5)}$$

therefore $l = 0, 1, 2, 3, \ldots (n-1)$.

Thus the electron can have only discrete values of the angular momentum. Thus like E the L (angular momentum) is also quantized (conserved); This quantization is ~~called~~ described by l.

l - orbital quantum number. This expression for the angular momentum is identical to that obtained in Bohr's theory, provided K is replaced by $\sqrt{l(l+1)}$

* Interpretation of m_l (m)

when the atom is placed in external magnetic field. If the field along the z-axis.

$$L_z = m_l \frac{h}{2\pi} = m\frac{h}{2\pi}$$

$m = 0, \pm 1, \pm 2, \pm 3 \ldots$

m describes the quantization of the orientation of $\vec{L}$ in a magnetic field

Thus the solution of the Schroedinger Equation gives much more information just than just the energies. And from the wave function ψ we can calculate other atomic properties that were not possible in the Bohr–Sommerfeld theory.

Question: Write the wave-function for the ground state of hydrogen atom and calculate the most probable and the average distance of the electron from the Nucleus. Hence discuss the characteristics of the state of the atom.

Sol. The ground state of one-electron atom, $n=1$, $l=0$, $m=0$, $Z=1$

$$\psi_{1,0,0} = \underbrace{R_{1,0}(r)}\ \underbrace{\Theta_{0,0}(\theta)}\ \underbrace{\Phi_{0}(\phi)}$$

$$= 2\left(\frac{Z}{a_0}\right)^{3/2} \times e^{-\frac{Zr}{a_0}} \times \frac{1}{\sqrt{2\pi}} \times \frac{1}{\sqrt{2}}$$

$$= \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

* Magnetic Quantum number (m or m_l)

As we know that the orbital quantum no. l determines the magnitude of the of the electron's angular momentum $\vec{L}$. It is a vector quantity that describes the direction and magnitude of $\vec{L}$ of the electron.

What possible significance can a direction in space have for a hydrogen atom? The answer is that when a electron is revolving about a nucleous makes a current loop and has a magnetic field like a magnetic dipole.

Therefore an electron possesses angular momentum interacts with the external magnetic field $\vec{B}$. Therefore, the magnetic quantum no (m_l) specifies the direction of $\vec{L}$ by determining the component of $\vec{L}$ in the magnetic field. This phenomenon is called the space quantization.

Let if the magnetic field $\vec{B}$ is in the direction to the parallel to the z-axis, the component of $\vec{L}$ in this direction is given by as

$$L_z = m_l \hbar, \quad m_l = 0, \pm 1, \pm 2 \ldots$$

(Space quantization)

The possible values of m_l for a given value of l lies from $+l$ to $-l$ (including 0).

Therefore, the total no. of possible orientation of $\vec{L}$ in a magnetic field is $(2l+1)$.

Here, if $l = 0$, $L_z = 0$,
$l = 1$, $L_z = \hbar, 0, -\hbar$
$l = 2$, $L_z = 2\hbar, \hbar, 0, -\hbar, -2\hbar$.
and ~~seen~~ so on ...

The space quantization of the angular momentum L $(l = 2)$ is shown in ~~Fig~~ the below figure.

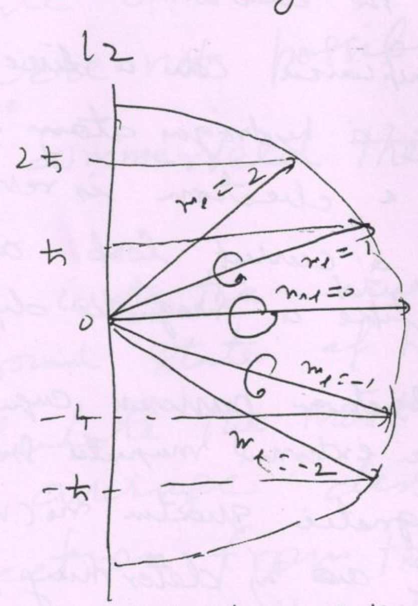


Fig: Space quantization of the orbital angular momentum $(L = 2)$.

Relativistic correction

The total energy (E_n) of the electron in the ground state in H_2 atom is given by

$$E_n = -\frac{\mu e^4 Z^2}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = -\frac{\mu Z^2 e^4}{8 \epsilon_0^2 h^2 n^2} \quad \text{—(1)}$$

(Non-relativistic energy)

Now if consider the relativistic correction, the non-relativistic relation of ... as given by

$$\cancel{E = \frac{p^2}{2m} + E_{pot}} \quad \text{—(2)} \qquad E = \frac{p^2}{2m} + E_{pot} \quad \text{—(2)}$$

$$E = c\sqrt{m_0^2 c^2 + p^2} - m_0c^2 + E_{pot} \quad \cancel{(3)} \quad (17)$$

For the electron in the H_2 atom, the velocity v of the electron is still small compared to the velocity of c, which means that E_{kin} is m_0c^2 or $\frac{p^2}{m_0c^2}$.

We can therefore expand the square root of (3) into the power series as

$$\left(1 + \frac{p^2}{m_0^2 c^2}\right)^{1/2} = 1 + \frac{1}{2}\cdot\frac{p^2}{2m_0c^2} - \frac{1}{8}\frac{p^4}{m_0^4 c^4} + \cdots$$

which gives the energy expression ~~(2)~~ as of eqn (3) as

$$E = m_0 c^2\left(1 + \frac{1}{2}\frac{p^2}{2m_0c^2} - \frac{1}{8}\frac{p^4}{m_0^4c^4}\right) + \cdots - \cancel{m_0c^2} + E_{pot}$$

$$= \left(\frac{p^2}{2m_0} + E_{pot}\right) - \frac{p^4}{8m_0^3c^2} + \cdots = (4)$$

$$= E_{nr} - \Delta E_r \quad (4)$$

Now we can obtain the quantum mechanical expectation value of this correction by putting $p = -i\hbar\nabla$ which leads the expression as

$$\Delta E_r = \frac{\hbar^4}{8m_0^3c^2}\int \psi^*_{n,l,m}\nabla^4\psi_{n,l,m}\,d\tau \quad (5)$$

putting the value of ψ of H_2 atom into eqn (5)

We get, $\Delta E_r = + E_{nr}\frac{Z^2\alpha^2}{n^2}\left(\frac{3}{4n} - \frac{1}{l+1/2}\right)$ (6)

Where $\alpha = \frac{e^2}{\ldots} = 7.297\times10^{-3} = \frac{1}{137}$ (7)

where α is called the Sommerfeld's fine structure constant

Now, the total energy of an Eigen-~~state~~ state for the H_2 atom is

$$E_{n,l} = -R_y \frac{z^2}{n^2}\left(1 - \frac{\alpha^2 z^2}{n}\left(\frac{3}{4n} - \frac{1}{l+\frac{1}{2}}\right)\right) \quad (8)$$

where $R_y \rightarrow$ Rydberg constant $= \frac{m_0 e^4}{8\epsilon_0^2 h^2}$

and Eqn (8) total energy of the H_2 atom.

The. Electron Spin

Several Experiments such as the Stern-Gerlach (S.G) experiment, or the ~~and~~ the fine-structure of the spectral lines, or the anomalous Zeeman effect results that the electron must have an additional characteristic property (besides charge $-e$ and mass m_e), which was called electron spin. This spin must cause an additional magnetic moment (μ_s) in addition to the orbital magnetic moment μ_l. This is already postulated by Fermi, before it could be Experimentally confirmed

The Stern-Gerlach Experiment:

In 1925, Uhlenbeck and Goudsmith proposed that each electron spins while revolving about nucleus and has quantized spin angular momentum and being an electrically charged body (also ...

spin magnetic moment. This proposal was successfully correlated the spectral data for both unperturbed and perturbed complex atoms. And was successfull to interpret the results of the Stern-Gerlach Experiment.

In this experiment, a beam of neutral atoms or molecules, collimated by slits S_1 and S_2 and is allowed to pass through a non-uniform magnetic field $\vec{B}$ (as shown in the Fig —)

The atoms or molecules are deflected by the magnetic force $\vec{F}$ and given by as

$$\vec{F} = \vec{\nabla}(\vec{m}\cdot\vec{B}) \quad \text{—} (1)$$

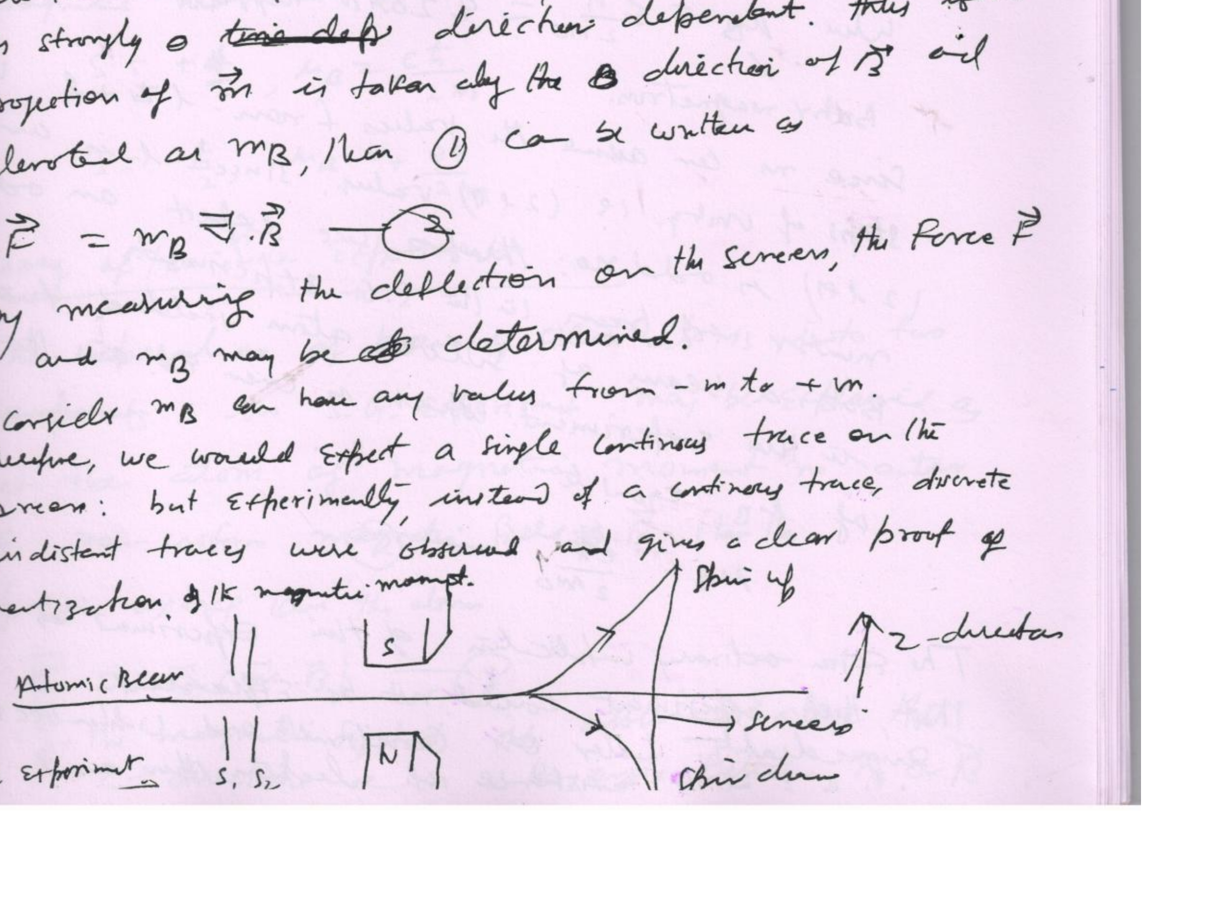
where $\vec{m}$ – magnetic moment vector.

Here the direction of $\vec{B}$ varies slowly but the magnitude of $\vec{B}$ is strongly ~~time dep~~ direction dependent. Thus if the projection of $\vec{m}$ is taken along the direction of $\vec{B}$ and denoted as m_B, then (1) can be written as

$$\vec{F} = m_B \vec{\nabla}\cdot\vec{B} \quad \text{—} (2)$$

by measuring the deflection on the screen, the force $\vec{F}$ and m_B may be determined.

Classically m_B can have any values from $-m$ to $+m$. Therefore, we would expect a single continuous trace on the screen: but experimentally, instead of a continuous trace, discrete equidistant traces were observed, and gives a clear proof of quantization of the magnetic moment.



Ex– S.G. Experiment

(20) Since the magnetic moment vector $\vec{m}$ appeared to assume certain discrete directions in space, therefore it is called the space quantization.

Now the magnetic moment $\vec{m}$ of the charged particle is related to the angular momentum $\vec{L}$ by classically,

$$\vec{m} = -\frac{e}{2m_0}\vec{L} \quad (3)$$

Since L has $(2l+1)$ component, we may expect the projection of $\vec{m}$ in a fixed direction, such as on $\vec{B}$ and can be written as

$$m_B = -\frac{e\hbar}{2m_0} m \quad (4)$$

$$m_B = -\mu_B m \quad (4)$$

when $\mu_B = \frac{e\hbar}{2m_0} = 9.20\times10^{-20}$ J/Tesla.

Bohr magnetron.

Since m can assume the values from $-l$ to $+l$ with steps of unity. i.e. $(2l+1)$ values. Since l is an integer $(2l+1)$ is odd no: therefore we expect an odd number of traces in the S.G. experiment.

But a beam of silver atom yielded two traces in this experiment. which is even no. and the value of μ_B equal to

$$\mu_B = \frac{e\hbar}{2m_0} \quad (5)$$

The extra-ordinary implication of this experiment is that, this experiment could not be explained immediately. Later on Goudsmit and Uhlenbeck [illegible] the existance of electron spin and intrinsic magnetic moment provided an explanation for this experiment. On the basis of this theory the silver atom in the S-state has two projections possible in space, namely

$$\mu_B = \pm \frac{e\hbar}{2m_0} \quad \text{—— (6)}$$

The positive and negative signs signify the orientation of the magnetic moment in the space i.e. up and down

Goudsmith and Uhlenbeck assumed that the electron has an intrinsic (or spin) angular momentum, but this is not easy to measure directly as the magnetic moment.

Hence it is convenient to associate spin S with the magnetic moment as

$$S = +\frac{\hbar}{2}, \quad \mu_B = -\frac{e\hbar}{2m_0}$$

$$S = -\frac{\hbar}{2}, \quad \mu_B = +\frac{e\hbar}{2m_0}$$

Theory of the S.G. Experiment

The separation of beam of silver atoms into two components in S.G. Experiment may be explained as let the atom of magnetic moment m enter a non-uniform magnetic field $\vec{B}$. Then the force acting on the atom

$$\vec{F} = \vec{\nabla}(\vec{m}\cdot\vec{B}) \quad \text{—— (7)}$$

If the magnetic field is assumed along the z-direction and θ is the angle between $\vec{m}$ & $\vec{B}$

Then
$$F = m\cos\theta \frac{\partial B}{\partial z} \quad \text{--- (2)}$$
classically θ can have all possible values but quantum mechanically, according the space quantization, it can have only descrete values.

as the electron enters θ in the non-uniform magnetic field $\vec{B}$) then

acceleration $a_z = \frac{F}{M_0}$ --- (3)

$M_0 \to$ mass of the atom.

$\ell \to$, if L is the length of the magnetic field, u is the velocity of the atom along the direction of the beam, then time taken by the atom in $\vec{B}$

$$t = \frac{L}{u} \quad \text{--- (4)}$$

the displacement along the z-direction

$$z = \frac{1}{2} a_z t^2$$

$$= \frac{1}{2} \cdot \frac{F}{M_0} \cdot \left(\frac{L}{u}\right)^2$$

$$= \frac{1}{2} \frac{\left(m\cos\theta \cdot \frac{\partial B}{\partial z}\right)}{M_0} \left(\frac{L}{u}\right)^2$$

$$= \frac{1}{2} m\cos\theta \left[\frac{L^2}{M_0 u^2}\right] \frac{\partial B}{\partial z} \quad \text{--- (5)}$$

quantum mechanically, and according to the space quantization $\cos\theta = \pm 1$,

$$z = \pm \frac{1}{2} \frac{mL^2}{M_0 u^2} \frac{\partial B}{\partial z} \quad \text{--- (6)}$$

(6) gives the two directions for spin half particle, which is observed in the S.G. experiments