Hydrogen and Hydrogen like atoms / or ions

Hydrogen atom consists of a positively charged nucleus and an electron moving about it. positive ions containing one electron bound to a nucleus of charge $+Ze$ such as He^+, Li^{+2}, B^{+3} etc may be treated Quantum mechanically like H-atom. These are called H-like ions

Potential Energy and Hamiltonian for H atom.

H like systems are characterised by a spherically symmetric potential energy. According to coulomb's law, the force between a pair of charged particles is

$$F = \frac{-Ze^2}{r} \quad \text{—— (1)}$$

[Ze - charge of nucleus
e = charge of electrons
r = distance between nucleus & e^-]

The schrodinger equation for H-like atom

$$\frac{-h^2}{8\pi^2\mu} \nabla^2 \psi + \hat{V}\psi = E\psi \quad \text{—— (2)}$$

$$\frac{-h^2}{8\pi^2\mu} \nabla^2 \psi - \frac{Ze^2}{r}\psi = E\psi \quad \text{—— (3)}.$$

μ = reduced mass $= \frac{Mm_e}{M+m_e}$ M = mass of nucleus, m_e = mass of e^-

since $M >>> m_e$. $\mu \simeq m_e$.

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Replacing ∇^2 in terms of spherical polar coordinates

$$\frac{-h^2}{8\pi^2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\left(\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi$$

$$-\frac{Ze^2\psi}{r} = E\psi \quad \text{---} (4)$$

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{r}\right)\psi = 0 \quad \text{---} (5)$$

$\psi = \psi(r,\theta,\phi)$

solving the schrodinger Equation

$\psi(r,\theta,\phi)$ can be expressed in terms of 3 independent functions $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$ ——— (6)

substituting for ψ in equation (5)

$$\Theta\Phi\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+R\Phi\frac{1}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+ R\Theta\frac{1}{r^2\sin^2\theta}\frac{d^2\Phi}{d\phi^2}+\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{r}\right]R\Theta\Phi = 0 \quad (7)$$

Multiplying equ (7) by $\frac{r^2\sin^2\theta}{R\Theta\Phi}$

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2\sin^2\theta}{h^2}\left[E+\frac{Ze^2}{r}\right]+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = 0 \quad \text{---} (8).$$

In equation (8) Φ is isolated from R & Θ, ie when Φ changes, the other terms do not change,

$$\therefore \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \quad \text{---} (9)$$

Now, substituting ~~from~~ equation (9) ~~and~~ in (8) and deviding by $\sin^2\theta$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{r}\right)+\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{m^2}{\sin^2\theta} = 0 \quad (10)$$

In equation (10) R and Θ parts are separated. The first two terms have only r terms and the last two terms

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The sum of first two terms is set equal to constant β. & the sum of the 3 & 4 terms is therefore equal to $-\beta$.

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{r}\right)R=\beta R \quad (11)$$

ie
$$r^2\frac{d^2R}{dr^2}+2r\frac{dR}{dr}+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{r}\right)R=\beta R$$

$\div r^2$
$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\left\{\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{r}\right]-\frac{\beta}{r^2}\right\}R=0 \quad (12)$$

and
$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{m^2\Theta}{\sin^2\theta}=-\beta\Theta$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta=0 \quad (13)$$

The complete solution of Equation (5) comprises the solutions of equations (9), 12, and 13.

The Φ equation:

$$\Phi(m)=\frac{1}{\sqrt{2\pi}}e^{im\phi} \qquad m=0,\pm1,\pm2\ldots$$

m is magnetic quantum number. It is called a magnetic quantum number, because in the presence of magnetic field, the states having different m values have different energies.

The Θ equation:

$$\Theta_{l,m}(\theta)=NP_l^m\cos\theta$$

$P_l^m\cos\theta$ = associated legendre function.

$$N = \text{Normalization constant} = \left[\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2}$$

$$\& \; P_l^m(x)=\frac{1}{2^l l!}(1-x^2)^{|m|/2}\frac{d^{l+|m|}}{dx^{l+|m|}}(x^2-1)^l$$

l can assume 0, 1, 2, ... and

or azimuthal Quantum number. The product of $\Theta_{l,m}(\theta) \cdot \Phi_m(\phi)$ is called spherical harmonics. $Y_{l,m}(\theta,\phi)$. These are also called angular functions.

The 'r' equation:

Since $\beta = l(l+1)$ equation (12) (radial equation) can be written as

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[\frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r}\right) - \frac{l(l+1)}{r^2}\right]R = 0 \quad \text{(14)}$$

Changing the variables for mathematical convenience, the asymptotic equation and its solution can be obtained

Let $\rho = \frac{2Zr}{na_0}$; $a_0 = \frac{h^2}{4\pi^2\mu e^2}$

and $n^2 = \frac{-2\pi^2 m Z^2 e^4}{h^2 E}$

$$\therefore E = \frac{-2\pi^2 \mu Z^2 e^4}{n^2 h^2}$$

since $r = \frac{\rho n a_0}{2Z}$

$$R(r) = R\left(\frac{na_0\rho}{2Z}\right)$$

$$\frac{dR}{dr} = \frac{2Z}{na_0}\frac{dR}{d\rho} \text{ and}$$

$$\frac{d^2R}{dr^2} = \left(\frac{2Z}{na_0}\right)^2\frac{d^2R}{d\rho^2} \text{ and}$$

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

$$\left(\frac{2Z}{na_0}\right)^2\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\left(\frac{2Z}{na_0}\right)^2\frac{dR}{d\rho} + \left[-\frac{1}{4}\left(\frac{2Z}{na_0}\right)^2 + \frac{n}{\rho}\left(\frac{2Z}{na_0}\right)^2 - \left(\frac{2Z}{na_0}\right)^2\frac{l(l+1)}{\rho^2}\right]R = 0$$

using the relations $\frac{8\pi^2\mu E}{h^2} = \frac{-16\pi^4\mu^2 e^4 Z^2}{n^2 h^4}$

$$= \frac{-1}{4}\left(\frac{2Z}{na_0}\right)^2$$

and $\frac{8\pi^2\mu Z e^2}{h^2 r} = \frac{4Z^2}{na_0^2\rho} = \frac{n}{\rho}\left(\frac{2Z}{na_0}\right)^2$.

Equation (14) be converted as

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right]R = 0 \quad \text{(15)}$$

Solving the radial Equation :

For large values of ρ the equation reduces to.

$$\frac{d^2R}{d\rho^2} - \frac{R}{4} = 0 \quad \text{———} \quad (16)$$

The solution being

$$R = Ae^{-\rho/2} \quad \text{———} \quad (17)$$

For small values of ρ,

$$\frac{l(l+1)}{\rho^2} >> \frac{\lambda}{\rho} \text{ and } \frac{1}{4} .$$

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2}R = 0 .$$

Its solution is $\quad R = \rho^l$ ——— (18)

The radial function R for all values of ρ has the general form

$$R = \rho^l L(\rho) e^{-\rho/2} \quad \text{———} \quad (19)$$

$L(\rho)$ is a polynomial – a power series in ρ known as Laguerre polynomial.

Differenating R twice and rearranging,

$$\rho L'' + 2(l+1) - \rho) L' + (n-l-1)L = 0. \quad \text{———} \quad (20).$$

Solution to this appears in the form of associated Laguerre polynomial, expressed as $L_{n+l}^{2l+1}(\rho)$.

$$L(\rho) = e^{\rho} \frac{d^{n+l}}{d\rho^{n+l}} \left(\rho^{n+l} e^{-\rho}\right)$$

and $\cancel{L^{2l+1}}$

$$L_{n+l}^{2l+1}(\rho) = \frac{d^{2l+1}}{d\rho^{2l+1}} \left[L(\rho) \right].$$

The normalization factor for the R function is

$$N = \left[\left(\frac{\rho}{r}\right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3} \right]^{1/2}$$

The normalised radial function $R_{nl}(\rho)$ is

$$R_{nl}(\rho) = N\rho^l L_{n+l}^{2l+1}(\rho) e^{-\rho/2} \quad \text{(22)}$$

$$n-l-1 = (n+l) - (2l+1)$$

$n-l-1$ represents the degree of polynomial which must be an integer or zero.

For $n-l-1 = 0$.

$$n = l+1.$$

For lowest value of $n = 1$ when $(l=0)$

$$n+l > 2l+1 \text{ or}$$
$$n > l+1$$

Acceptable solution to radial equation exist, for discrete values of n and l. n can be $1, 2, 3 \ldots$
l can be $0, 1, 2 \ldots (n-1)$.

and $l < n$

Radial wave functions for different values of n and l:

$n=1,\ l=0$.

$$R_{10}(\rho) = N\rho^0 L_{1+0}^{0+1}(\rho) e^{-\rho/2}$$
$$= N L_1^1(\rho) e^{-\rho/2}$$

Here $L_1^1 = \frac{d}{d\rho}\left(e^\rho \frac{d}{d\rho} \rho e^{-\rho}\right)$

$$= \frac{d}{d\rho}(1-\rho) = -1.$$

$$N = \left[\frac{(1-0-1)!}{2\times 1 \times \{[1+0]!\}^3}\left(\frac{2Z}{a_0}\right)^3\right]^{1/2}$$

$$= -2\left(\frac{Z}{a_0}\right)^{3/2}$$

$$R_{10}(\rho) = (-2)\times(-1)\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$$

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

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$n=2,\ l=0$

$$R_{20} = \frac{1}{\sqrt{8}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$$

$n=2,\ l=1$

$$R_{21} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} r\, e^{-Zr/2a_0}$$

. etc.

Energy eigen value:

$$E = -\frac{2\pi^2 \mu Z^2 e^4}{n^2 h^2}.$$

Complete wave function:

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,\Theta_{lm}(\theta)\,\Phi_{m}(\phi)$$
$$= R_{nl}(r)\,Y_{l,m}(\theta,\phi)$$

For $n=1, l=0, m=0$

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$n=2, l=0, m=0$

$$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$$

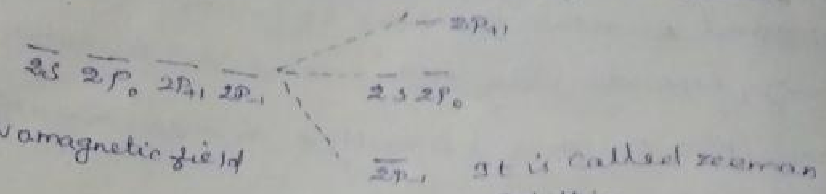
$n=2, l=1, m=0$

$$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(Z/a_0\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta$$

$n=2, l=1, m=\pm 1$

$$\psi_{2,1\pm1} = \frac{1}{\sqrt{64\pi}}\left(Z/a_0\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\sin\theta\, e^{\pm i\phi}$$

$(2l+1)$ fold degeneracy in the absence of magnetic field is split into $(2l+1)$ different energies in the presence of magnetic field, each characterised by a 'm' value.



It is called zeeman splitting

Atomic orbitals:

The wave functions of H-like atoms are called atomic orbitals.

For H-like atoms the energy depends on n only and is independent of l and m, hence orbitals having the same n and differing l and m values are degenerate

$[1s] < [2s, 2P] < [3s, 3P, 3d] < \cdots$

i.e $[1s] < [2s, 2P_{+1}, 2P_0, 2P_{-1}] < \cdots$

Except when $m=0$, the wavefunctions (atomic orbitals) of H-like atoms are complex due to the presence of terms like $e^{\pm im\phi}$. These cannot be drawn in real space. However, by taking linear combinations of wavefunctions having the same l values, we can obtain good solutions.

This three p orbitals with $m=0, +1, -1$; designated as p_0, p_{+1}, p_{-1} have the following angular factors (apart from numerical factor) associated with them.

$$p_0 \sim \cos\theta$$

$$p_{+1} \sim \sin\theta\, e^{i\phi}$$

$$p_{-1} \sim \sin\theta\, e^{-i\phi}.$$

Combinations of p_{+1} and p_{-1} atomic orbitals can be written as $2p_{+1} + 2p_{-1} = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r\sin\theta\, e^{-Zr/2a_0} (e^{i\phi}$

$$= \frac{2}{\sqrt{64\pi}} \left(\frac{z}{a_0}\right)^{5/2} r \sin\theta \cos\phi \, e^{-zr/2a_0}$$

$$\frac{1}{\sqrt{2}} (2P_{+1} + 2P_{-1}) = \frac{1}{\sqrt{32\pi}} \left(\frac{z}{a_0}\right)^{5/2} x \, e^{-zr/2a_0}.$$

$x = r\sin\theta\cos\phi$.
$y = r\sin\theta\sin\phi$.
$z = r\cos\theta$

This is called $2P_x$ orbital.

similarly

$$\frac{1}{i\sqrt{2}} (2P_{+1} - 2P_{-1}) = \frac{1}{\sqrt{32\pi}} \left(\frac{z}{a_0}\right)^{5/2} y \, e^{-zr/2a_0}$$

This is called $2P_y$ orbital.

physical representation of orbitals:

For $l = 0$, the function ψ_{ns} are functions of r only; that is, the radial part of wave function. It does not depend on θ or ϕ and so the wavefunctions are spherically symmetric.

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

As the principal quantum number n increases, the function ψ_{ns} oscillates as directed by its polynomial part and 'nodal' points appear where $\psi = 0$. The number of nodes for s function is $(n-1)$.

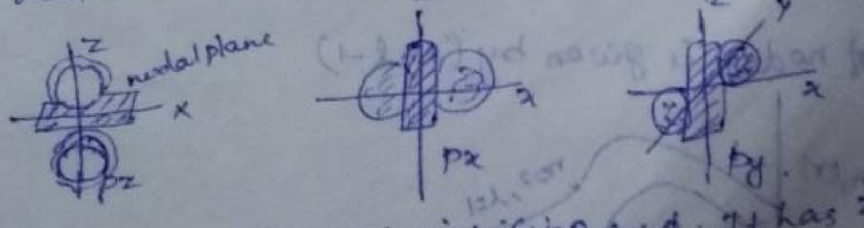
$$\psi_{3s} = \frac{1}{81\sqrt{3\pi}} \, z^{3/2} [27 - 18zr + 2z^2r^2] \, e^{-zr/3}.$$

No node for ψ_{1s}.

1 node for ψ_{2s}, 2 nodes for ψ_{3s} etc.

polar plot of s orbital is independent θ or ϕ and is spherical.

The $2P_z$ function is independent of ϕ and is symmetric with respect to z axis. The xy plane is the nodal plane.



The $2P_x$ function contains $\sin\theta\cos\phi$. It has 2 spheres along the x axis with yz plane as nodal plane. similarly $2P_y$ has $\sin\theta\sin\phi$. It has 2 spheres along y axis with xy plane

...nodal plane.

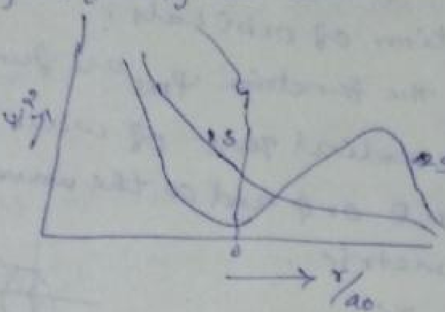
Probability Density:

ψ^2 represents the probability density of the electron

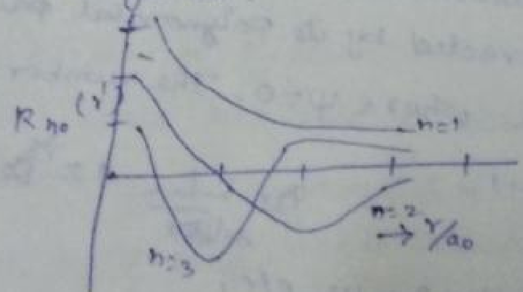
ie, ψ^2 represents the charge per unit volume - (electron density)

For example ; $\psi_{1s}^2 = \frac{1}{\pi a_0^3} e^{-2r/a_0}$.

ψ^2 is the probability per unit volume and not the actual probability of finding the electron at any point.



The radial plot of ψ against r (or r/a_0) for different s functions is given:

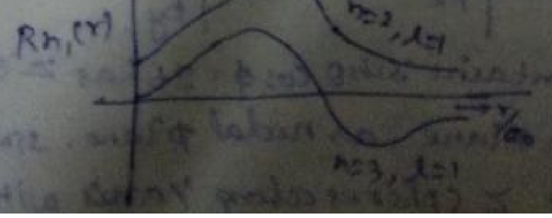


$$\psi_{2s} = \frac{1}{\sqrt{32\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}.$$

* node appears where $\psi_{2s} = 0$.

ie $2 - \frac{r}{a_0} = 0$, $r = 2a_0 = 2$ a.u (a.u = atomic unit)

For $l \neq 0$, $\psi = 0$ at $r = 0$ because of r^l factor. The number of nodes is given by $(n-l-1)$



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The angular or polar plot of ψ against θ or ϕ is a way of representing ψ or $Y(\theta, \phi)$ with $R(r)$ chosen as constant. polar plots represent the physical shape of the orbital under consideration.

The actual probability is given by

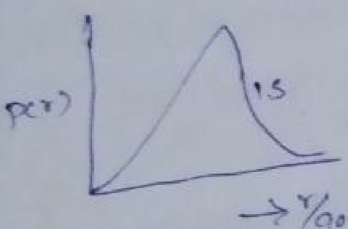
$\psi^2 d\tau$ where $d\tau = r^2 dr \sin\theta \, d\theta \, d\phi$.

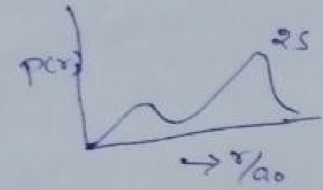
The radial distribution $(P(r))$ is obtained by integrating $\psi^2 d\tau$ over all angles of θ and ϕ and not over r.

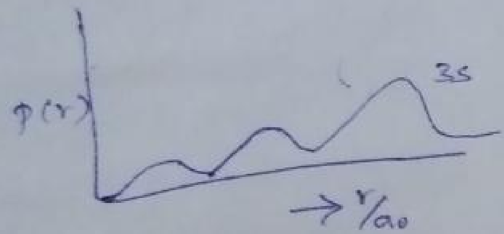
$$P(r)dr = R^2(r)\, r^2 dr = \int_0^{\pi} \Theta^2(\theta) \sin\theta \, d\theta \int_0^{2\pi} \Phi^2(\phi) d\phi$$

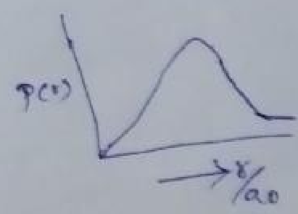
$$= r^2 R^2(r) dr.$$

$$P(r) = r^2 R^2(r)$$









Similarly angular probability distribution is obtained by integrating $\psi^2 d\tau$ over all values of r for θ with ϕ constant or for ϕ with θ constant.