Antisymmetric Wave-function of electrons (fermions).

Ψ - Non - Observable

But,

$|\Psi|^2$ - Probability density is observable

$\downarrow$

So, exchange symmetry requires that prob. density (and all observable properties) to be unaffected by the exchange of any 2 particles.

Note: e^- are identical particles ie. it is not possible to distinguish one from the other. ie. Cannot label the particles. (No physical process exist which would be affected by the exchange of the 2 particles). [Exchange Symmetry]

For N particles,

$$P(\dots, x_a, \dots x_b, \dots) = |\Psi(\dots, x_a, \dots, x_b, \dots|^2$$

prob density

Where $1 \leq a, b \leq N$

and all the values of x_a and x_b.

In order for this observable prob. density to have exchange symmetry, it must obey the relation:

$$P(\dots, x_a, \dots x_b, \dots) = P(\dots, x_b, \dots x_a, \dots)$$

In terms of wave function, this means

$$|\Psi(\dots, x_a, \dots, x_b, \dots)|^2 = |\Psi(\dots, x_b, \dots, x_a, \dots)|^2$$

In order for this to be true, the wave function must only differ by an overall phase factor upon exchanging the particles,

$$\Psi(\dots, x_b, \dots, x_a, \dots) = e^{i\phi}\Psi(\dots, x_a, \dots, x_b, \dots)$$

Where ϕ is some real no. between 0 and 2π.

For bosons $\phi = 0$ — Symmetric wave function

Fermions (e^-) $\phi = \pi$ — Anti symmetric ψ

$\therefore e^{i\pi} = -1$

$\therefore \psi(\ldots, x_b, \ldots, x_a, \ldots) = -\psi(\ldots, x_a, \ldots, x_b, \ldots)$

Why fermions have phase factor of π

e^- must rotate by 4π for identity or rotate by 2π & exchange.

Fermions have $1/2$-integer spin

$\therefore$ A rotation of the angular momentum by 2π results in a phase change by -1

$\uparrow \xrightarrow{180°} \downarrow$

$+1/2 \qquad -1/2$

Pauli exclusion principle (from Hydrogen-like atom)

$$\psi(x_a, x_b) = -\psi(x_b, x_a)$$

$$\psi(x_a, x_b) = \frac{1}{\sqrt{2}}\left(\psi_a(x_a)\psi_b(x_b) - \psi_a(x_b)\psi_b(x_a)\right)$$

Normalising factor (reduce total prob to 1)

Linear Combination

$$\psi(x_b, x_a) = \frac{1}{\sqrt{2}}\left(\psi_a(x_b)\psi_b(x_a) - \psi_a(x_a)\psi_b(x_b)\right)$$

$\therefore \psi(x_a, x_b) = -\psi(x_b, x_a)$ is satisfied

$\psi(x_a, x_b)$ can be written as:

$$\frac{1}{\sqrt{2}}\begin{vmatrix} \psi_a(x_a) & \psi_b(x_a) \\ \psi_a(x_b) & \psi_b(x_b) \end{vmatrix}$$

For N fermions

$$\psi(x_a, x_b, \ldots x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_a(x_a) & \psi_b(x_a) & \cdots & \psi_N(x_a) \\ \psi_a(x_b) & \psi_b(x_b) & \cdots & \psi_N(x_b) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_a(x_N) & \psi_b(x_N) & \cdots & \psi_N(x_N) \end{vmatrix}$$

Slater determinant

Now, Consider

$$A = \begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix} \xrightarrow{\text{row exchange}} A' = \begin{vmatrix} 3 & 4 \\ 1 & 2 \end{vmatrix}$$

$\det A = 4 - 6 = -2$

$\det A' = 6 - 4 = 2$

$\therefore$ Slater determinant is antisymmetric upon exchange of 2 electrons.

Note: All electrons are taken to be similar in Q.M / Physics / Chemistry / Science.

Implying that 2 Slater determinants are equal is saying that 2 electrons with the same Ψ occupy the same position x.

1 1
1
1

Note: A Slater determinant corresponds to a single stick diagram $\Rightarrow$ 1

ie. a single value for Ψ and x

↑ Specify quantum state $(n, l, m, \underbrace{m_s}_{s})$

↳ Specify position.

1 slater determinant = 1 e^- on stick diagram.

For 2 Slater determinant to be equal (ie. 2 electrons occupy same x having same Ψ)

$\rightarrow A = -A' \rightarrow 2 = -2$

the slater determinant must be 0 $\rightarrow \begin{vmatrix} 0 & 0 \\ 0 & 0 \end{vmatrix} = \begin{vmatrix} 0 & 0 \\ 0 & 0 \end{vmatrix}$

Yielding $\Psi = 0$ for both e^- in same x having same Ψ

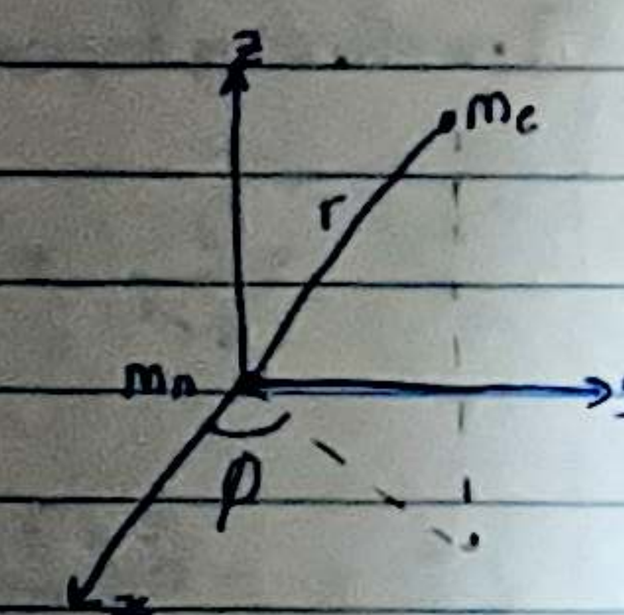
Since prob density $= |\Psi|^2$

$\Rightarrow$ probability of $2e^-$ having same $\Psi\ (n, l, m, m_s)$ occupying same position $x = |0|^2 = 0$

↳ Pauli Exclusion principle.

The hydrogen Atom

$$\vec{F} = \frac{-Ze^2}{4\pi\varepsilon_0 r^2}\,\underbrace{\hat{r}}_{\text{unit vector in direction of } F} \longrightarrow \text{Force is central (ie directed at 1 point)}$$



$$V = \frac{Ze^2}{4\pi\varepsilon_0}\int \frac{1}{r^2}\,dr = \frac{-Ze^2}{4\pi\varepsilon_0 r}$$

To deal with internal motion, reduced mass μ is introduced

$$\mu = \frac{m_e m_n}{m_e + m_n}$$

↳ Mass subjected to $V(E_p)$ and its coords. are one particle relative to an ptle

Hamiltonian for internal motion (E_{Total})

$$\hat{H} = \underbrace{\frac{-\hbar^2}{2\mu}}_{\text{Kinetic}}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \rightarrow V \text{ is a function of the } r \text{ coord only} \rightarrow \text{1-particle central force problem.}$$

∇^2: 2nd partial derivative (Laplacian operator)

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

Transforming laplacian operator to spherical coords.

$$\nabla^2 = \frac{\partial}{\partial r^2} + \frac{2}{r}\frac{\partial}{\theta r} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\phi^2}$$

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

Orbital angular momentum in spherical coords.

$$\text{So, } \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2\hbar^2}\hat{L}^2$$

$$\hat{H} \text{ becomes } = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}\hat{L}^2 + V(r)$$

In Classical mechanics, particles subjected to central force has its angular momentum conserved.

In Quantum mechanics to have quantised energy & angular momentum the set of eigenfunctions of $\hat{H}$ also be eigenfunctions of $\hat{L}^2$

Gives an indication of the extent to which a binary operation fails to be commutative ← Unique characteristic of a parameter & function

Commutator $[\hat{H}, \hat{L}^2]$ must vanish to allow for quantisation.

Involves only θ and ϕ not r

Commutator Identities

$x^y = x[x,y]$ conjugate

$[y,x] = [x,y]^{-1}$

In group G with elements g, h

$[g,h] = g^{-1}h^{-1}gh \equiv$ group identity iff $(gh = hg)$ commute

$$[\hat{H}, \hat{L}^2] = [\hat{T}, \hat{L}^2] + [\hat{V}, \hat{L}^2]$$

$$[\hat{T}, \hat{L}^2] = \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{2mr^2}\hat{L}^2, \hat{L}^2\right]$$

$$= -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}, \hat{L}^2\right] + \frac{1}{2m}\left[\frac{1}{r^2}\hat{L}^2, \hat{L}^2\right]$$

Involves only θ and ϕ not r

$\therefore$ it commutes with every operator involving only r

$\therefore [\hat{T}, \hat{L}^2] = 0$

Since any operator commutes with itself and since $\hat{L}^2$ does not involve r and V is a function of r only

$[\hat{V}, \hat{L}^2] = 0$

$$[\hat{H}, \hat{L}^2] = 0 \text{ if } V = V(r)$$

~~So, $\Psi(r,\theta,\phi) = R(r)Y_l^m(\theta,\phi)$ $l = 0, 1, 2, \ldots$ $|m| \leq l$~~

Spherical harmonic

$\hat{H}$ commutes with $\hat{L}^2$ when V is independent of θ, ϕ

Not Mentioned → $\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$, Since L_z does not involve r and V is a function of r only,

$\Rightarrow [\hat{H}, \hat{L}_z] = 0$ if $V = V(r)$

Eigenfunctions for central force problem

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

denote eigenfunction

$\hat{L}^2\psi = l(l+1)\hbar^2\psi \quad l = 0, 1, 2, \dots$

$\hat{L}_z^2\psi = m\hbar\psi \quad m = -l \quad -l+1, \dots l$

Schrodinger Equation becomes

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) + \frac{1}{2mr^2}\hat{L}^2\psi + V(r)\psi = E\psi$$

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) + \frac{\overbrace{l}^{n\text{-principal quantum no.}}+(l+1)\hbar^2}{2mr^2}\psi + V(r)\psi = E\psi \quad (1)$$

The eigenfunctions of $\hat{L}^2$ are the spherical harmonics $Y_l^m(\theta, \phi)$

Complete Set of orthogonal functions on the sphere and may be used to represent functions defined on the Surface of a sphere.

and Since $\hat{L}^2$ does not involve r, Y_l^m can be multiplied by an arbitrary function of r and still have eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$

$$\therefore \psi = R(r)Y_l^m(\theta, \phi) \quad -(2)$$

(2) in (1) and dividing by Y_l^m we get O.D.E for unknown function $R(r)$.

$$-\frac{\hbar^2}{2m}\left(R'' + \frac{2}{r}R'\right) + \frac{l(l+1)}{2mr^2}R + V(r)R = ER(r) \quad -(3)$$

Thus for any 1-particle problem with a spherically symmetric $V(r)$, the Stationary state wave function are (2) where the radial factor $R(r)$ Satisfies (3)

Back to λ

Put $a = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$

(3) becomes
$$R'' + \frac{2}{r}R' + \left[\frac{8\pi\varepsilon_0 E}{a e^2} + \frac{2Z}{ar} - \frac{l(l+1)}{-r^2}\right]R = 0 \quad (3')$$

For: Soln of the radial eqn

For large values of r
(3') becomes

$$R'' + \frac{8\pi\varepsilon_0 E}{a e^2}R = 0 \quad (r \to \infty)$$

Solving 2nd order O.D.E gives

$$e^{\pm\left(\frac{-8\pi\varepsilon_0 E}{a e^2}\right)^{1/2} r}$$

For $E>0$, quantity under $\sqrt{}$ is -ve and the factor multiplying r is imaginary

$$R(r) \sim e^{\pm i\frac{\sqrt{2\mu E}r}{\hbar}}, \quad E \geq 0 \longrightarrow$$ This does not give Complete radial factor for +ve energies

↓

Behaviour as free particle

behaviour of R for large values of r
(assymptotic behavior of the functio)

For $E \geq 0$, the +ve energy eigenfunctions are called continuum eigenfunctions
(Not normalisable)

For bound state ($E<0$) → Remain localised in atom.

$\Psi \to 0$ as $x \to \pm\infty$ ∴ quantity under $\sqrt{}$ is +ve

For wave function to remain finite as $r \to \infty$, -ve sign is used

$$⑥ - R(r) = e^{-Cr} K(r) \qquad C = \sqrt{\frac{8\pi\epsilon_0 E}{a e^2}}$$

$$r^2K'' + (2r - 2Cr^2)K' + [(2Za^{-1} - 2C)r - l(l+1)]K = 0 \quad - ⑤$$

power series → in form of $K = \sum_{k=0}^{\infty} C_k r^k$

If C_s is the first non-zero coeff

∴

$$K = \sum_{k=s}^{\infty} C_k r^k \qquad C_s \neq 0$$

put $j = k-s \to b_j \Rightarrow b_j \equiv C_{j+s}$

$$K = \sum_{j=0}^{\infty} C_{j+s} r^{j+s} = r^s \sum_{j=0}^{\infty} b_j r^j \qquad b_0 \neq 0$$

$$K(r) = r^s M(r), \quad M(r) = \sum_{j=0}^{\infty} b_j r^j \qquad b_0 \neq 0$$

Evaluating K & K'' and substituting into ⑤

$$\to r^2M'' + [(2s+2)r - 2Cr^2]M' + [s^2 + s + (2Za^{-1} - 2C - 2Cs)r - l(l+1)]M = 0$$

put $r=0$

$M(0) = b_0 \quad M'(0) = b_1 \quad M''(0) = 2b_2$ ⟵ Power Series Soln.

$$b_0(s^2 + s - l^2 - l) = 0$$

↓

not zero

$$\Rightarrow s = l, \quad s = (-l-1)$$

⑥ becomes

$$R(r) = e^{-Cr} r^s \sum_{j=0}^{\infty} b_j r^j$$

↓

Behaves for small r as $b_0 r^s$

For $s = l$, $R(r)$ behave properly at origin

For $s = -l-1$, $R(r) \propto \frac{1}{r^{l+1}}$ for small r

Since $l = 0, 1, 2, \ldots$ $s = -l-1$ means the radial factor in the wave function infinite at the origin (rejected) for $S = l$

$$R(r) = e^{-Cr} r^{l} M(r)$$

With $S = l$

$$rM'' + (2l + 2 - 2Cr)M' + (2Za^{-1} - 2C - 2Cl)M = 0$$

$$M(r) = \sum_{j=0}^{\infty} b_j r^j$$

$$M' = \sum_{j=0}^{\infty} j b_j r^{j-1} = \sum_{j=1}^{\infty} j b_j r^{j-1} = \sum_{k=0}^{\infty} (k+1) b_{k+1} r^k$$

$$= \sum_{j=0}^{\infty} (j+1) b_{j+1} r^j$$

$$M'' = \sum_{j=0}^{\infty} j(j-1) b_j r^{j-2} = \sum_{j=1}^{\infty} j(j-1) b_j r^{j-2} = \sum_{k=0}^{\infty} (k+1)kb \ldots$$

$$= \sum_{j=0}^{\infty} (j+1) j b_{j+1} \ldots$$

Subs in (7)

$$\sum_{j=0}^{\infty} \Big[j(j+1) b_{j+1} + 2(l+1)(j+1) b_{j+1} + \left(\frac{2Z}{a} - 2C - 2Cl \ldots\right.$$

Putting $r^j = 0$

$$b_{j+1} = \frac{2C + 2Cl + 2Cj - 2Za^{-1}}{j(j+1) + 2(l+1)(j+1)} b_j \quad - (8)$$

For large r

$$R(r) \sim e^{-Cr} r^{l} e^{2Cr} = r^{l} e^{Cr}$$

ensure that $\Psi = 0$ as $r \to \infty$

Let last term in power series expansion be $b_k r^k$. Then $b_{k+1}, b_{k+2}, \ldots$ disappear

the fraction multiplying b_j in the expansion must cancel out when $j = k$

$$2C(k + l + 1) = \cancel{\frac{2Z}{a}}\ 2Za^{-1}, \quad k = 0, 1, 2, \ldots$$

$$n = k + l + 1, \quad n = 1, 2, 3$$

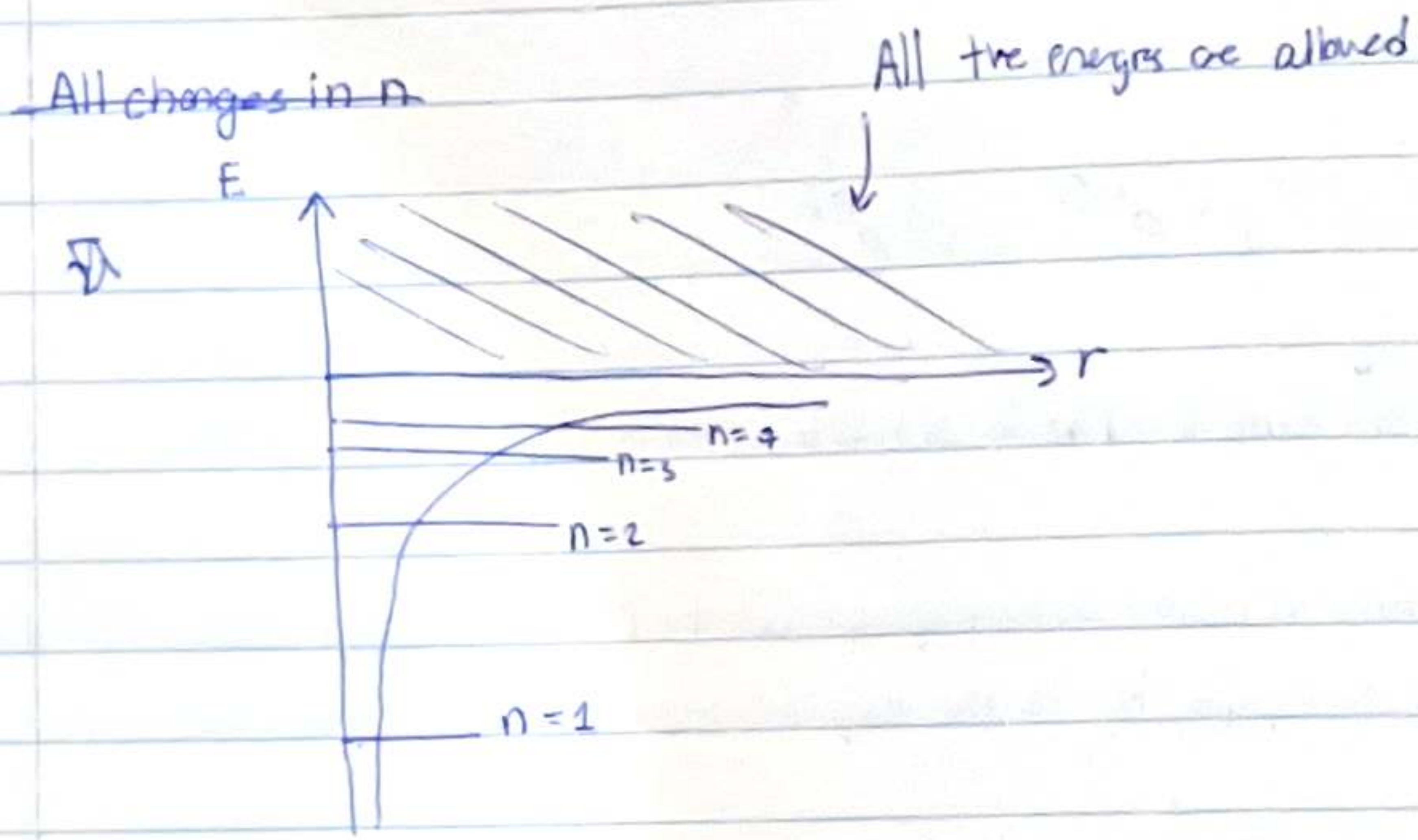
$\boxed{l \leq n - 1}$ → l ranges from 0 to $n-1$

$$Cn = Za^{-1} \qquad C = \left(\frac{-8\pi\varepsilon_0 E}{ae^2}\right)^{1/2}$$

(9) $$E = -\frac{Z^2}{n^2} \frac{e^2}{8\pi\varepsilon_0 a} = -\frac{Z^2 \mu e^4}{8\varepsilon_0^2 n^2 h^2}$$

Bound-state energy level for hydrogen ~~like~~ atom (discrete)

~~All changes in n~~



* All changes in n are allowed in light absorption and emission.

Wave number of spectral lines of H atom are

$$\bar{\nu} = 1/\lambda = \frac{\nu}{c} = \frac{E_2 - E_1}{hc} = \frac{e^2}{8\pi\varepsilon_0 a h c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Rydberg constant for hydrogen.

Degeneracy

For the bound states the energy depends only on n but wave function depend of n, l and m (with their specific allowed values)

Hydrogen atoms with diff l & m but same n have the same energy. The energy levels are degenerate. (except n=1 where $l, m = 0$)

For a given value of n, we can n different value of l

Bound-state H-atom wave function

Using (8) & (9)

$$b_{j+1} = \frac{2Z}{na} \frac{j + l + 1 - n}{(j+1)(j+2l+2)} b_j$$

highest power of r in $M(r) = \sum_j b_j r^j$ is $k = n - l - 1$

Use of $C = Z/na$ in $R(r)\, e^{-Cr} r^l M(r)$

$$R_{nl}(r) = r^l e^{-Zr/na} \sum_{j=0}^{n-l-1} b_j r^j$$

$$\psi_{nlm} = R_{nl}(r)\, Y_l^m(\theta, \phi) = R_{nl}(r)\, S_{lm}(\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

The radial function is 0 at $r = \infty$, $r = 0$ for $l \neq 0$ and at values of r that ~~are~~ cancel $M(r)$

root of $M(r) = 0$ ~~one-root~~ & the

Thus aside from origin & infinity there are $n - l - 1$ nodes in $R(r)$

For G.S, H-like atom
↳ $n=1$, $l=0$, $m=0$

$$R_{10}(r) = b_0 e^{-Zr/a}$$

$$|b_0|^2 \int_0^\infty e^{-2Zr/a} r^2 dr = 1$$

$$R_{10}(r) = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

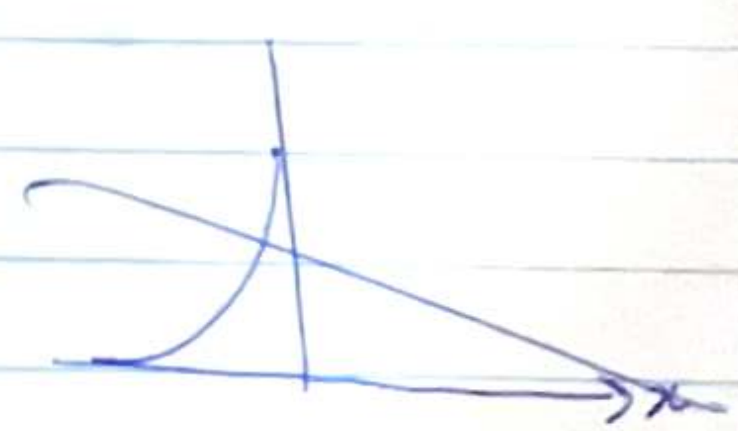
Multiplying by $Y_0^0 = 1/\sqrt{4\pi}$

We have as the G.S wave function

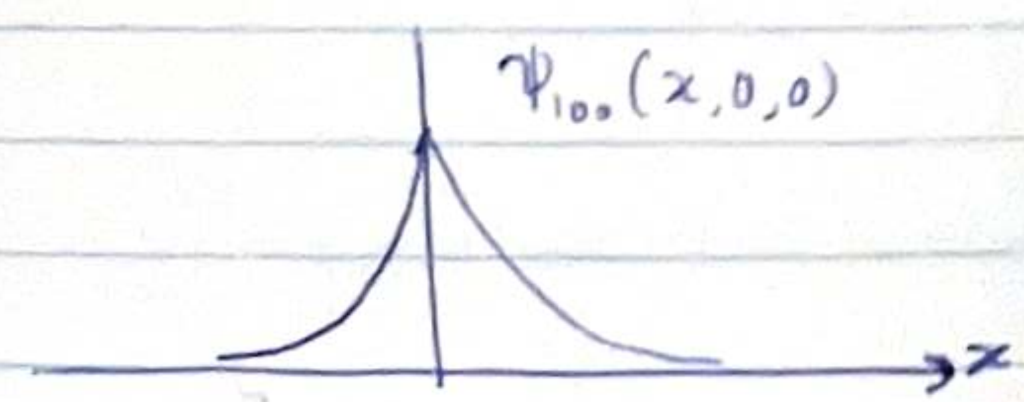
$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(Z/a\right)^{3/2} e^{-Zr/a}$$

$$\psi_{100}(x,0,0) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-\frac{Z|x|}{a}}$$

$r = \sqrt{x^2+y^2+z^2}$ on x axis, $y=0, z=0$ $r = \sqrt{x^2} = |x|$



$\psi_{100}(x,0,0)$



Although ψ_{100} is continuous at the origin, the slope of the tangent to the curve is +ve at the left of the origin but −ve at its right. Thus $\partial\psi/\partial x$ is discontinuous at the origin
(Wave function has a cusp at the origin)
↳ V becomes ∞ at origin

$\psi_{100} \rightarrow \psi_{1s}$ or $1s$
(value of n; value of l)

Wave functions for $n=2$
ψ_{200} ψ_{21-1}, ψ_{210}, ψ_{211}

$$R_{1s} = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

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

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

r^l Makes radial function 0 except for s states

$$2P_{-1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a} \sin\theta\, e^{-i\phi}$$

$$2P_0 = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a}\right)^{5/2} re^{-Zr/2a} \cos\theta$$

$$2P_1 = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a} \sin\theta\, e^{i\phi}$$

~~The radial~~

~~The radial distribution function~~

Bond State energy level for hydrogen atom.

$$E = -\frac{z^2 \mu e^4}{n^2 8 \varepsilon_0^2 h^2}$$

For H atom $z = 1$, $n = 1$ (Ground State energy)

$$E = \frac{\mu e^4}{8 \varepsilon_0^2 h^2} \leftarrow$$

$$\mu_H = \frac{m_e m_p}{m_e + m_p} = 0.9994557\, m_e$$

$$E = \frac{0.9994557\, m_e \times e^4}{8 \varepsilon_0^2 h^2}$$