

(2.1e)

$(k_1 a)$ is a zero of the l th-order spherical Bessel function. Since $J_l(x)$ are oscillatory, each having infinite number of zeros.

Let β_{nl} be the n th zero of the l th spherical Bessel function, then

$$k_1 a = \beta_{nl}$$

$$k_1 = \frac{\beta_{nl}}{a}$$

$$\frac{2m E_{nl}}{\hbar^2} = \frac{\beta_{nl}^2}{a^2}$$

$$E_{nl} = \frac{\hbar^2}{2ma^2} \beta_{nl}^2$$

This is the required eigenvalue formula of the problem.

Since the Neumann fns $N_l(x)$ diverge at the origin, and since the wavefn ψ_{nlm} are required to be finite everywhere in space, the functions

$N_p(x)$ are unacceptable solutions to the problem. Hence only the spherical Bessel functions $J_p(x)$ contribute to the eigenfns. of the free particle.

The first few spherical Bessel and Neuman functions are and, also their shapes are displayed in fig below.

$$J_0(x) = \frac{\sin x}{x}$$

$$J_1(x) = \frac{\sin x}{x} - \frac{\cos x}{x}$$

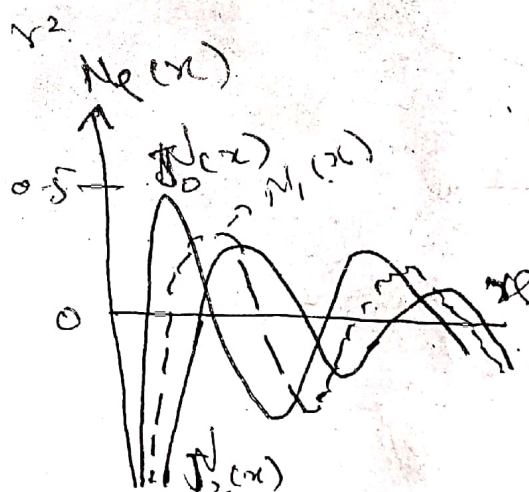
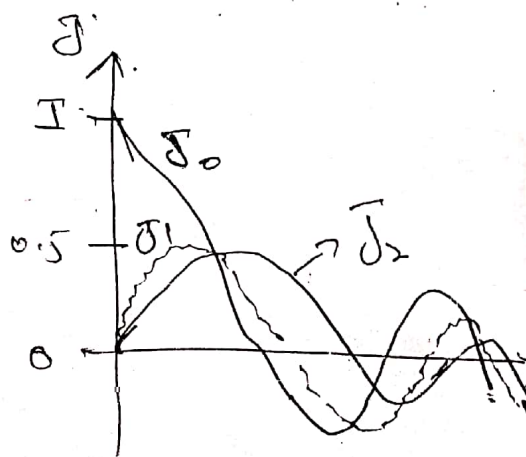
$$J_2(x) = \left(\frac{3}{x^3} - \frac{1}{x} \right) \sin x - \frac{3 \cos x}{x^2}$$

⇒ Similarly

$$N_0(x) = -\frac{\cos x}{x}$$

$$N_1(x) = -\frac{\cos x}{x^2} - \frac{\sin x}{x}$$

$$N_2(x) = -\left(\frac{3}{x^3} - \frac{1}{x} \right) \cos x - \frac{3}{x^2} \sin x$$



One can observe that the amplitude of the fns becomes smaller and smaller as x^0 increases.

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The corresponding wavefns. are

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi).$$

where

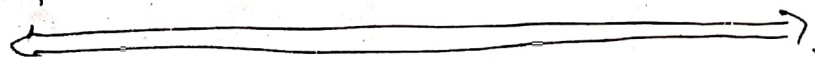
$$R_{n\ell}(r) = A_{n\ell} J_{\ell} \left(\frac{\beta_{n\ell} r}{a} \right) \quad \therefore K_1 = \frac{\beta_{n\ell}}{a}.$$

Therefore

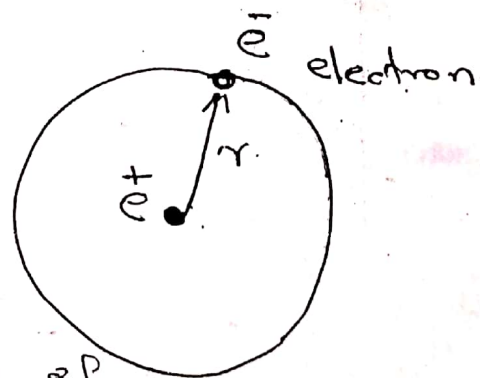
$$\psi_{n\ell m}(r, \theta, \phi) = A_{n\ell} J_{\ell} \left(\frac{\beta_{n\ell} r}{a} \right) Y_{\ell m}(\theta, \phi)$$

The constant $A_{n\ell}$ can be determined using the normalization condition.

The HYDROGEN ATOM:-



The hydrogen atom consists of an electron revolving around a motionless proton.



The charges of the two particles are equal but opposite in sign. The motion of the electron can be considered as the

motion of a particle moving in the field produced by the proton. From the Coulomb's law the potential energy is

$$V(r) = -\frac{e^2}{r}$$

Since the potential is centrally symmetric, the wavefn. of the revolving electron is of the form

$$\begin{aligned} \psi_{nlm} &= A_{nl} R_{nl}(r) Y_{lm}(\theta, \phi) \\ &= A_{nl} \frac{u_{nl}(r)}{r} C_{lm} P_{lm}(\cos\theta) e^{im\phi} \end{aligned}$$

where 'u' is the solution of the differential equation $\rightarrow \frac{d^2 u}{dr^2} + \frac{2m_e(E-V)}{\hbar^2} u - \frac{l(l+1)}{r^2} u = 0$

$$\frac{d^2 u}{dr^2} + \frac{2m_e}{\hbar^2} \left[E + \frac{e^2}{r} - \frac{\hbar^2 l(l+1)}{2m_e r^2} \right] u = 0$$

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

In order to solve this equ, let us introduce new variables ρ and Z such that

$$E = -\frac{\rho^2 m_e e^4}{2\hbar^2}$$

and

$$r = \frac{\hbar^2 Z}{m_e e^2}$$

Now.

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$$\frac{du}{dr} = \frac{du}{dz} \cdot \frac{dz}{dr}$$

Putting the value of $\frac{dz}{dr} = \frac{m_e e^2}{\hbar^2}$

$$\frac{du}{dr} = \frac{m_e e^2}{\hbar^2} \frac{du}{dz}$$

$$\frac{d^2 u}{dr^2} = \left(\frac{m_e e^2}{\hbar^2} \right)^2 \frac{d^2 u}{dz^2}$$

In terms of the new variables,
equ. (2) can be expressed as.

$$\left(\frac{m_e e^2}{\hbar^2} \right)^2 \frac{d^2 u}{dz^2} + \frac{2m_e}{\hbar^2} \left[\frac{-P^2 m_e e^4}{2\hbar^2} + \frac{m_e e^2 e^2}{\hbar^2 z} - \frac{\hbar^2 l(l+1) m_e^2 e^4}{2m_e \hbar^4 z^2} \right] u = 0$$

$$\frac{d^2 u}{dz^2} + \left[-P^2 + \frac{2}{z} - \frac{l(l+1)}{z^2} \right] u = 0 \quad \text{--- (3)}$$

For large z , equ (3) can be written as.

$$\frac{d^2 u}{dz^2} - P^2 u = 0 \quad \text{--- (4)}$$

for $|z| \rightarrow \infty$

The solutions are.

$$e^{-pz} \text{ and } e^{pz}$$

So the general sol of equ. (3) can now be written as.

$$u(z) = \omega(z) e^{-pz} + \kappa(z) e^{pz}$$

Since $e^{pz} \rightarrow \infty$, as $z \rightarrow \infty$.

therefor. the acceptable asymptotic solution of the problem is.

$$u(z) = \omega(z) e^{-pz}$$

Now

$$\frac{du}{dz} = \frac{d\omega}{dz} e^{-pz} - p\omega e^{-pz}$$

$$\begin{aligned} \frac{d^2u}{dz^2} &= \frac{d^2\omega}{dz^2} e^{-pz} - p \frac{d\omega}{dz} e^{-pz} \\ &\quad - p \frac{d\omega}{dz} e^{-pz} + p^2\omega e^{-pz} \end{aligned}$$

Put these expressions in ~~equ~~ (3), we get

$$\frac{d^2\omega}{dz^2} - 2p \frac{d\omega}{dz} + \left[\frac{2}{z} - \frac{l(l+1)}{z^2} \right] \omega = 0$$

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Power Series Solution

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Let us expand $w(z)$ as a power series in z

$$w(z) = \sum_{i=0}^{\infty} a_i z^{i+\alpha}$$

where α can be determined as follows

$$\frac{dw}{dz} = \sum_{i=0}^{\infty} a_i (i+\alpha) z^{i+\alpha-1}$$

$$\frac{d^2w}{dz^2} = \sum_{i=0}^{\infty} a_i (i+\alpha)(i+\alpha-1) z^{i+\alpha-2}$$

Put these values in eqn (5), we get

$$\sum_{i=0}^{\infty} a_i \left[(i+\alpha)(i+\alpha-1) z^{i+\alpha-2} - z^l P(i+\alpha) z^{i+\alpha-1} + \left(\frac{2}{z} - \frac{l(l+1)}{z^2} \right) z^{i+\alpha} \right] = 0$$

Now compare the Coefficients of $z^{\alpha-2}$, when $i=0$

$$a_0(\alpha)(\alpha-1) - a_0 l(l+1) = 0$$

$$a_0 [\alpha(\alpha-1) - l(l+1)] = 0$$

Since $a_0 \neq 0$, therefore

$$\alpha(\alpha-1) - l(l+1) = 0$$

$$\alpha^2 - \alpha - l^2 - l = 0$$

$$(\alpha^2 - p^2) - (\alpha + p) = 0.$$

$$(\alpha + p)(\alpha - p) - (\alpha + p) = 0.$$

$$\Rightarrow \boxed{\alpha = -p} \text{ or } \boxed{\alpha = p+1}$$

If $\alpha = -p$, then

$$w(z) \rightarrow \infty, \text{ as } z \rightarrow 0$$

Ag. Therefore, we take $\alpha = p+1$

Again, Compare the Co-efficients of

$$\sum_{i=0}^{k+\alpha-2} z^i = k$$

$$a_k [(k+\alpha)(k+\alpha-1) - p(p+1)] z^{k+\alpha-2}$$

$$= a_k [2p(k+\alpha) - 2] z^{k+\alpha-1}$$

Put $k = k-1$, in right hand side we will get

$$a_k [(k+\alpha)(k+\alpha-1) - p(p+1)]$$

$$= a_{k-1} [2p(k+\alpha-1) - 2] z^{k-2}$$

So

⇒

$$a_k = \frac{2P(k+\alpha-1) - 2}{(k+\alpha)(k+\alpha-1) - l(l+1)} a_{k-1}$$

• $k = 1, 2, 3, \dots$

Since $\alpha = l+1$.

therefore

$$a_k = \frac{2P(k+l) - 2}{(k+l+1)(k+l) - l(l+1)} a_{k-1}$$

$$a_k = \frac{2[P(k+l) - 1]}{k^2 + 2kl + k} a_{k-1}$$

which is required recurrence relation.

From this relation, one can see that

$$\lim_{k \rightarrow \infty} \frac{a_k}{a_{k-1}} = \lim_{k \rightarrow \infty} \frac{2[P(k+l) - 1]}{(k^2 + 2kl + k)}$$

$$= \lim_{k \rightarrow \infty} \frac{2k[P(1 + \frac{l}{k}) - \frac{1}{k}]}{k^2 [1 + \frac{2l}{k} + \frac{1}{k}]}$$

$$\approx \frac{2P}{k} \rightarrow 0 \quad \text{as } \frac{1}{n} \rightarrow 0$$

Let us look at the ratio test of 4
 the series

$$e^{pz} = \sum_{k=0}^{\infty} Q_k$$

$$\lim_{k \rightarrow \infty} \frac{Q_k}{Q_{k-1}} = \lim_{k \rightarrow \infty} \frac{2p \cdot (k-1)!}{k! (2p)^{k-1}}$$

$$\approx \frac{2p}{k} \rightarrow 0$$

Note that $w(z)$ has the same convergence behaviour as that of e^{2pz}

So we can write

$$u(z) = w(z) e^{-pz}$$

$$\approx e^{2pz} e^{-pz}$$

$$u(z) = e^{pz}$$

where

$$e^{pz} \rightarrow \infty \text{ as } z \rightarrow \infty$$

e^{pz} must be terminated after a finite number of terms.

Let us terminate the series at

$$k = K_r$$

i.e

$$a_{K_r} = 0 \Rightarrow a_{K_r+p} = 0$$

$$p = 1, 2, 3, \dots$$

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a_{kr} will be zero when.

$$P(kr+l)-1 = 0$$

$$P = \frac{1}{kr+l} = \frac{1}{n}$$

where

$$n = kr+l$$

is the principle quantum number.

\Rightarrow

$$E_n = - \frac{P^2 m e e^4}{2 \hbar^2} = \frac{-m e e^4}{2 \hbar^2} \frac{1}{n^2}$$

$$E_n = - \frac{1}{2} \frac{e^2}{a n a}$$

where

$$a = \frac{\hbar^2}{m e^2} = 0.53 \text{ \AA}$$

is called Bohr radius.

So

$$E_n = \frac{E_1}{n^2}, \quad n = 2, 3, \dots$$

This is the famous Bohr formula.

The wavefn's for hydrogen are labeled by three quantum numbers (n, l, m).

$$\Psi_{nlm}(r, \alpha, \phi) = A_{nl} \frac{u_{nl}(r)}{r} Y_{lm}(\alpha, \phi)$$

$$= \frac{A_{nl}}{r} e^{-\rho z} \omega_{nl}(z) P_{lm}(\cos \alpha) e^{im\phi}$$

where

ω_{nl} is the polynomial of degree

$$K_r - l + \alpha = K_r - l + l + 1 \quad (\alpha = l + 1)$$

$$= K_r + 1$$

$$= n$$

when

$$n = 1, \quad l = 0, \quad m = 0$$

$$K_r = 1$$

$$a_1 = 0 \Rightarrow a_2 = a_3 = a_4 = \dots = 0$$

$$E_1 = - \frac{m_e e^4}{2 \hbar^2} = -13.6 \text{ eV}$$

This is the ground state energy of the hydrogen atom.

Eigenfunctions of Hydrogen Atom:

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Let us start with the eqn.

$$\frac{d^2 w}{dz^2} - 2P \frac{dw}{dz} + \left[\frac{2}{z} - \frac{l(l+1)}{z^2} \right] w = 0.$$

Now write

$$w(z) = t^{l+1} v(z)$$

where $t = \frac{2z}{n} = \frac{2r}{na_0}$

Then

$$\frac{dw}{dt} = (l+1)t^l v + t^{l+1} \frac{dv}{dt}$$

and $P = \frac{1}{n}$

$$\begin{aligned} \frac{d^2 w}{dz^2} &= l(l+1)t^{l-1} v + (l+1)t^l \frac{dv}{dt} \\ &+ (l+1)t^l \frac{dv}{dt} + t^{l+1} \frac{d^2 v}{dt^2} \end{aligned}$$

Therefore the equation above now can be expressed as:

$$t \frac{d^2 v}{dt^2} + [2(l+1) - t] \frac{dv}{dt} + (n - (l+1)) v = 0$$

Let us consider the Laguerre Polynomial L_q , which are the solutions of.