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# LAB ASSIGNMENT - 09

Answer (a):-

Since, TISE is of the form:-

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

Now, we have to determine the Laplace operator in spherical coordinate :-

$\because$ $x = r\sin\theta \cos\phi$
$y = r\sin\theta \cdot \sin\phi$
$z = r\cos\theta$

$\because$ $r^2 = x^2+y^2+z^2$

& $\tan\phi = y/x$

Thus Schrodinger eq$^n$ in Polar coordinate is:-

$$\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0\right]$$

This is schrodinger eq$^n$ in spherical coordinate.

(b)

Since, S.E in polar form is:-

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

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

Multiply by $r^2\sin\theta$:-

$$\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{\partial^2\psi}{\partial\phi^2}$$

$$+\frac{2mr^2\sin^2\theta}{\hbar^2}(E-V)\psi=0 \quad -(1)$$

$\because$ $\psi$ is $\psi(r,\theta,\phi)=R(r)\cdot P(\theta)\cdot\Theta(\phi)$. $-(2)$

Putting (2) in (1):-

$$\frac{1}{R(r)}\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{\sin\theta}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P(\theta)}{\partial\theta}\right)$$

$$+\frac{1}{\Theta(\phi)}\frac{\partial^2\Theta(\phi)}{\partial\phi^2}+\frac{2mr^2\sin^2\theta}{\hbar^2}(E-V)=0$$

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$$\therefore \frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{P}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)+\frac{2mr^2\sin^2\theta(E-V)}{\hbar^2}$$

$$= -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}$$

$\because$ L.H.S depends on $r$ & $\theta$ & R.H.S to $\phi$ but they are equal to same constant :-

$$\therefore \frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{P}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)+\frac{2mr^2\sin^2\theta}{\hbar^2}(E-V)=m^2$$

— (3)

dividing this by $\sin^2\theta$ :-

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}(E-V)=\frac{m^2}{\sin^2\theta}-\frac{1}{P\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)$$

— (4)

Now, again equating to a constant :-

$$\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}(E-V)=l(l+1)}$$

— (5)

This is radial part.

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$$4\left[\frac{m^2}{\sin^2\theta} - \frac{1}{P\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) = l(l+1)\right]$$

This is angular part.

(c)

Since, the radial Equation is:-

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}(E-V) = l(l+1) \quad \text{— (*)}$$

Let, $R = \frac{K}{r}$

$$\therefore \frac{dR}{dr} = \frac{\frac{dk}{dr}\times r - k}{r^2} \quad \text{— (1)}$$

$$4 \quad \frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = 2r\frac{dR}{dr} + r^2\frac{d^2R}{dr^2}$$

$$\left[\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{2dk}{dr} - \frac{2k}{r} + r^2\frac{d^2R}{dr^2}\right] \quad \text{— (2)}$$

Differentiating (1) again w.r.t R :-

$$\left[\frac{d^2(k/r)}{dr^2} = \frac{1}{r}\frac{d^2k}{dr^2} - \frac{2}{r^2}\frac{dk}{dr} + \frac{2k}{r^3}\right] \quad \text{— (3)}$$

Put (3) in (2) :-

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{2dk}{\cancel{r}} - \frac{2\cancel{k}}{\cancel{r}} + r\frac{d^2k}{dr^2} - 2\frac{d\cancel{k}}{\cancel{dr}} + \frac{2\cancel{k}}{\cancel{r}}$$

$$\left[\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = r\frac{d^2k}{dr^2}\right]$$

Put this in (*) :- r

$$\frac{r}{k}\left(r\frac{d^2k}{dr^2}\right) + \frac{2mr^2}{\hbar^2}(E-V) = l(l+1)$$

$$\frac{r^2}{k}\frac{d^2k}{dr^2} - \frac{2mr^2}{\hbar^2}(V-E) = l(l+1)$$

Multiply by $\frac{-\hbar^2}{2mr^2}$ on both side :-

$$\frac{-\hbar^2}{2m\cancel{k}}\frac{d^2k}{dr^2} + (V-E)k = l(l+1)k \times \frac{-\hbar^2}{2mr^2}$$

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{d^2k}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]k = Ek$$

Here $\Rightarrow \left[V_{effective} = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]$

$$\therefore \left[ -\frac{\hbar^2}{2m}\frac{d^2 k}{dr^2} + k\, V_{eff}(r) = kE \right] \quad \text{— (4)}$$

Now, replacing $r$ by $r_0$ bohr radius :-

$$\because \left[ a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \right]$$

Let, $r' = \frac{r}{a_0}$ where $r_0$ = above

Now, writing (4) in terms of $r'$ :-

$$\left[ \frac{dr'}{dr} = \frac{1}{a_0} \right]$$

$$\therefore \frac{dk}{dr} = \frac{dk}{dr'} \times \frac{dr'}{dr}$$

$$\left[ \frac{dk}{dr} = \frac{1}{a_0}\frac{dk}{dr'} \right]$$

Similarly, $$\frac{d^2k}{dr^2} = \frac{d}{dr}\left(\frac{dk}{dr}\right)$$

$$= \frac{1}{a_0}\frac{d}{dr}\left(\frac{dk}{dr'}\right)$$

$$= \frac{1}{a_0} \times \frac{d}{dr'}\left(\frac{dk}{dr'} \times \frac{1}{a_0}\right)$$

$$\left[ \frac{d^2k}{dr^2} = \frac{1}{a_0^2} \times \frac{d^2k}{dr'^2} \right] \quad \text{— (5)}$$

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$\because \ V_{eff} = V(r) + \dfrac{l(l+1)\hbar^2}{2mr^2}$

$$= \frac{-e^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2m(a_0 r')^2}$$

$$= \frac{-e^2}{4\pi\varepsilon_0 a_0 r'} + \frac{l(l+1)\hbar^2}{2m a_0^2 (r')^2}$$

$$= \frac{-e^2 \times me^2}{(4\pi\varepsilon_0)^2 \times \hbar^2 r'} + \frac{l(l+1)\hbar^2}{2\cancel{m} \times \frac{(4\pi\varepsilon_0)^2 \times \hbar^4}{m^{\cancel{2}} e^4} (r')^2}$$

$$V_{eff}(r') = \frac{-me^4}{(4\pi\varepsilon_0)^2 \hbar^2 r'} + \frac{l(l+1)\, me^4}{\hbar^2\, 2\, (4\pi\varepsilon_0)^2\, (r')^2}$$

$$\therefore V_{eff}(r') = \frac{me^4}{(4\pi\varepsilon_0^2)\hbar^2}\left[\frac{-1}{r'} + \frac{l(l+1)}{2(r')^2}\right] \quad -⑥$$

Now, using ⑤ & ⑥ writting ④

$$-\frac{\hbar^2}{2\cancel{m}} \times \frac{1}{(4\pi\varepsilon_0)^2 \times \hbar^4} \times m^2 e^4 \frac{d^2 k}{dr'^2} + \frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2} \times 2\left[\frac{-1}{r'} + \frac{l(l+1)}{2r'^2}\right]$$

$$= \frac{-me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{d^2}{dr'^2}k + \frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2} \times 2\left[\frac{-1}{r'} + \frac{l(l+1)}{2r'^2}\right]$$

$$\because \left[k(r') = k(r')\, G\right]$$

Energy of ground state hydrogen atom is :-

$$|E_1| = \frac{+me^4}{2\hbar^2(4\pi\varepsilon_0)^2}$$

$$\therefore \quad -\frac{d^2k(r')}{dr'^2} + 2\left[\frac{-1}{r'} + \frac{l(l+1)}{2(r')^2}\right] = k(r')E\left(\frac{2(4\pi\varepsilon_0)^2\hbar^2}{me^4}\right)$$

Let, $e = \frac{E}{|E_1|}$ & $v = \frac{-2}{r'} + \frac{l(l+1)}{r'^2}$

$\therefore$ Equ$^n$ becomes :-

$$\boxed{-\frac{d^2}{dr'^2}k(r') + v\,k(r') = e\,k(r')}$$

This is the radial equ$^n$ in dimensionless form.

(d) :-

$$V_{eff} = \underbrace{V}_{\substack{\text{classical} \\ \text{(coulombian) potential}}} + \underbrace{\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}}_{\text{centrifugal term}}$$

The ~~co~~ coulomb potential is attractive for opposite charges. Taking only the coulomb potential into account energy gets smaller the smaller r is.

The effective potential on the other hand is always positive making it repulsive.
Specifically, if you get close to the origin, $r \to 0$ the centripetal potential $V_{centripetal} \to +\infty$.
In physics systems tend to minimize their energy, so a position where potential energy is very large is not attractive for the system and you can say that the centripetal potential is keeping the wave function away from origin.

(f)

The dimensionless wave function $u(r)$ should be :-
zero , at $r=0$
zero , at $r=\infty$.

$\therefore$ $U(r)$ to be a acceptable wave function:
$U(r)=0$ on boundaries.

# 1 Discussion

1. This is the plot for effective potential and normal non-dimensionalised potential.

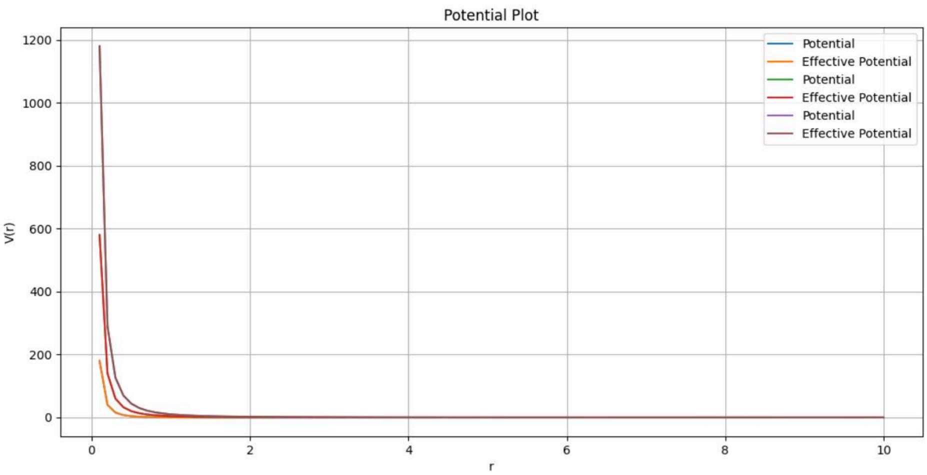
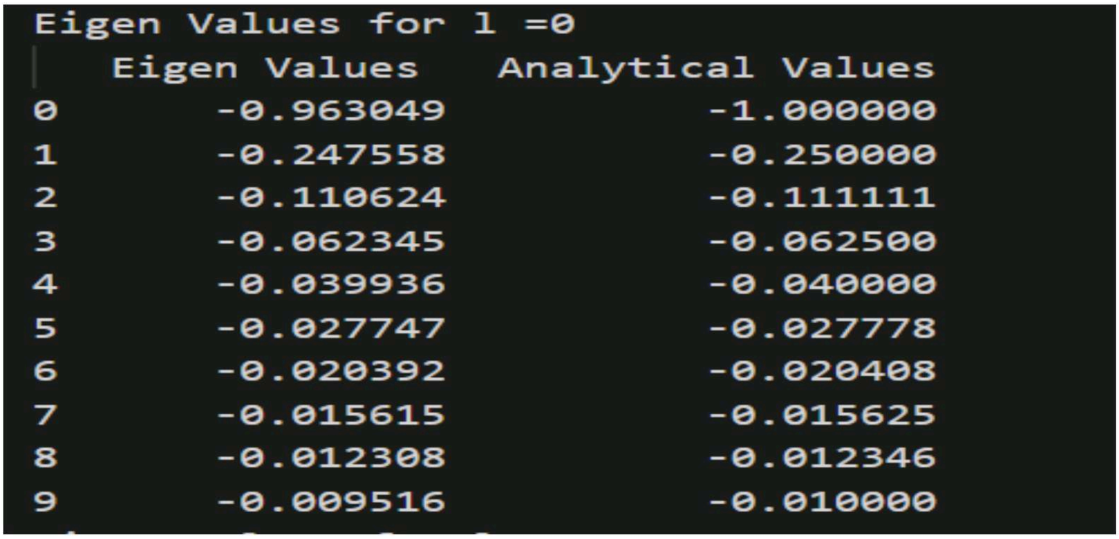



Figure 1:

2. These are the Eigen Values along with the non dimensional analytical eigen values for forst ten eigen states with $l = 0, 1, 2$ .



Eigen Values for l =0

| | Eigen Values | Analytical Values |
|---|---|---|
| 0 | -0.963049 | -1.000000 |
| 1 | -0.247558 | -0.250000 |
| 2 | -0.110624 | -0.111111 |
| 3 | -0.062345 | -0.062500 |
| 4 | -0.039936 | -0.040000 |
| 5 | -0.027747 | -0.027778 |
| 6 | -0.020392 | -0.020408 |
| 7 | -0.015615 | -0.015625 |
| 8 | -0.012308 | -0.012346 |
| 9 | -0.009516 | -0.010000 |

Figure 2:

Eigen Values for l =1

| | Eigen Values | Analytical Values |
|---|---|---|
| 0 | -0.250850 | -0.250000 |
| 1 | -0.111502 | -0.111111 |
| 2 | -0.062701 | -0.062500 |
| 3 | -0.040115 | -0.040000 |
| 4 | -0.027849 | -0.027778 |
| 5 | -0.020456 | -0.020408 |
| 6 | -0.015658 | -0.015625 |
| 7 | -0.012342 | -0.012346 |
| 8 | -0.009574 | -0.010000 |
| 9 | -0.006343 | -0.008264 |

Figure 3:

Eigen Values for l =2

| | Eigen Values | Analytical Values |
|---|---|---|
| 0 | -0.111144 | -0.111111 |
| 1 | -0.062531 | -0.062500 |
| 2 | -0.040024 | -0.040000 |
| 3 | -0.027795 | -0.027778 |
| 4 | -0.020421 | -0.020408 |
| 5 | -0.015634 | -0.015625 |
| 6 | -0.012330 | -0.012346 |
| 7 | -0.009606 | -0.010000 |
| 8 | -0.006458 | -0.008264 |
| 9 | -0.002583 | -0.006944 |

Figure 4:

3. This is the plot for the Radial Waveform for first four

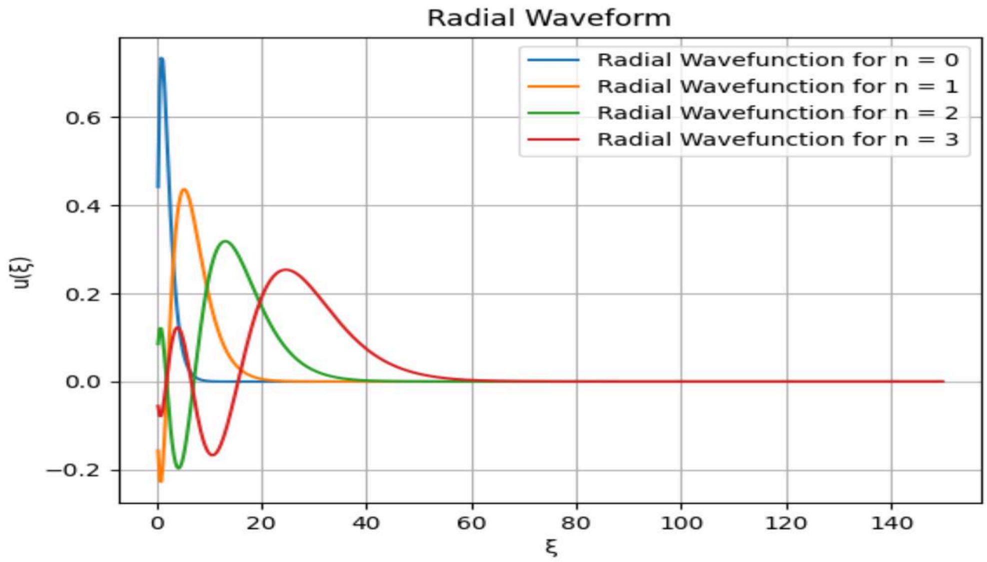



Figure 5:

4. In this part we are plotting the Probability Density for mentioned state along with $\xi$

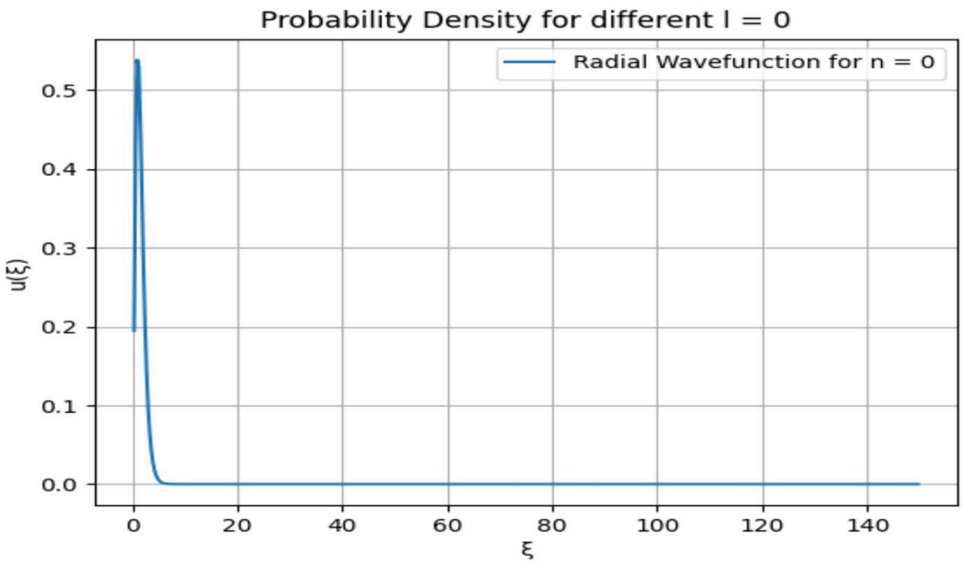



Figure 6:

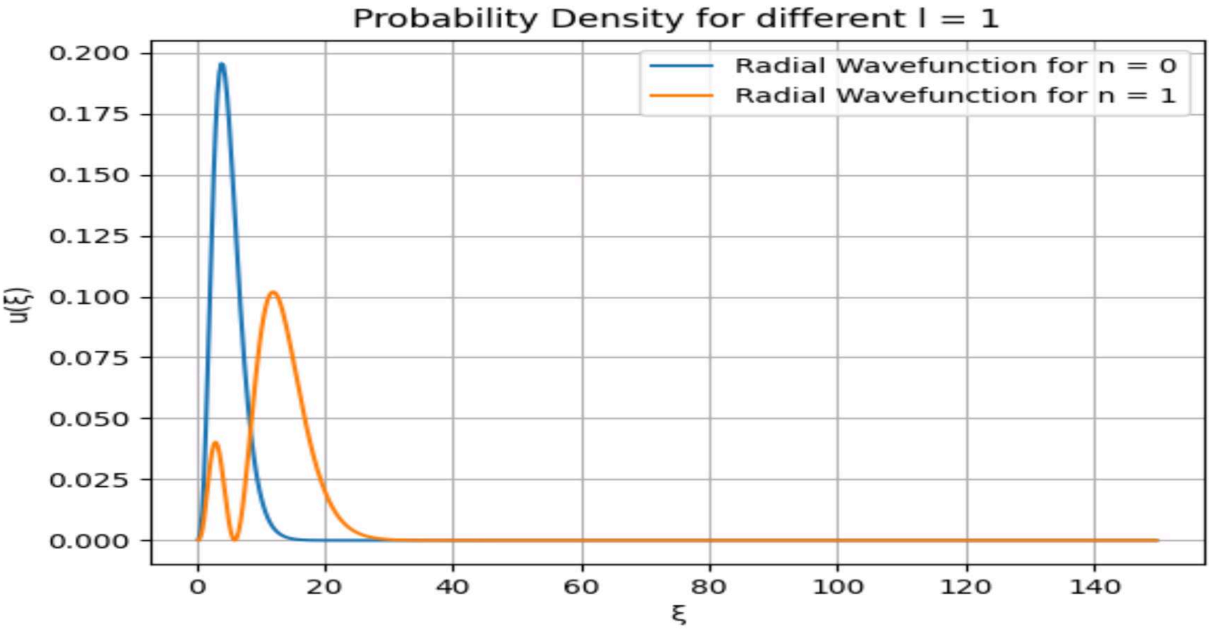



Figure 7:

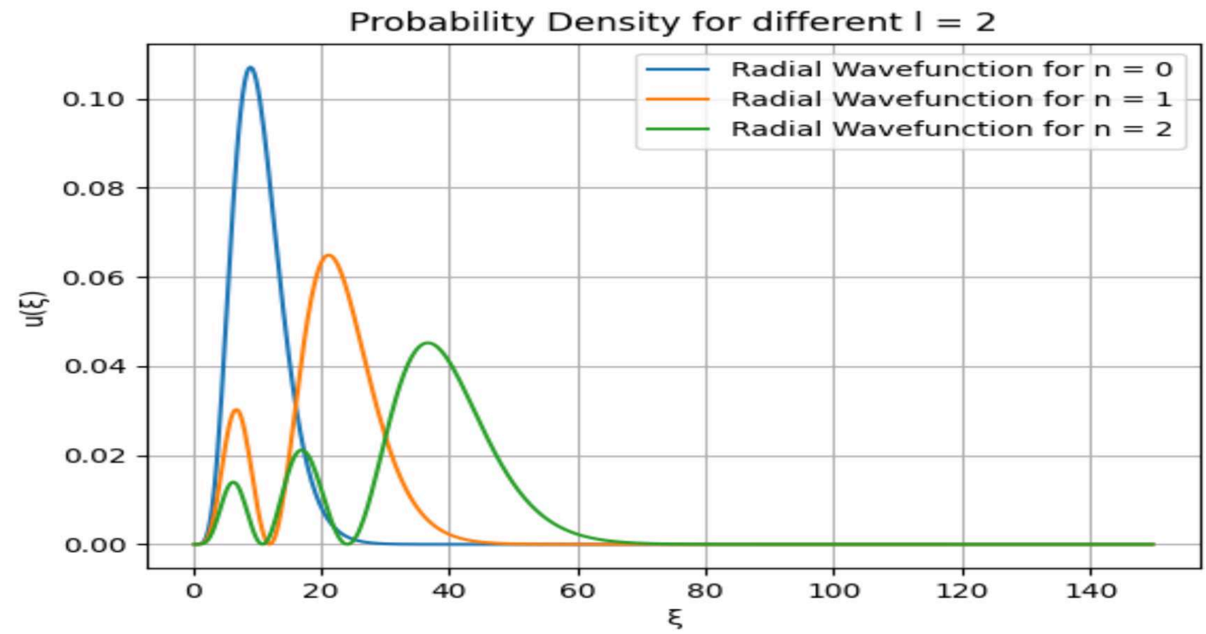



Figure 8:

| B.Sc.(Hons.) Physics<br>32221501<br>Teacher: Mamta | **S.G.T.B. Khalsa College**<br>**Quantum Mechanics (2022-23)**<br>**Lab Assignment # 9**<br>**H- atom using Finite Difference Method** | Due Date and Time :<br>11.09.2022, 11:59PM<br>Max. Marks : 20 |
|---|---|---|

The objective of this assignment is to

- numerically solve the radial part of Schrödinger Equation for "electron in H-atom" with Finite Difference method and determine the energy eigenvalues and corresponding normalised radial wavefunctions.

1. (10 marks) **Theory**

   (a) Write down the Schrödinger Equation for an electron in H-atom potential in spherical polar coordinates.

   (b) Use separation of variable method to separate this into angular and radial part. (Use $\psi_{n\ell m}(r, \theta, \phi) = \mathcal{R}_{n\ell}(r)\mathcal{Y}_{\ell m}(\theta, \phi)$ and take the separation constant as $\ell(\ell+1)$. )

   (c) Convert the Radial part of the Schrödinger Equation dimensionless form. Take $\mathcal{R}_{n\ell}(r) = \mathcal{K}_{n\ell}(r)/r$ and write the equation satisfied by $\mathcal{K}_{n\ell}(r)$. For this rescale $r$ by Bohr radius and the energies by $|E_1|$, $E_1$ being the ground state Bohr energy.

   (d) Discuss $V_{\text{eff}}(x)$ and its implications.

   (e) Write down the analytical expressions for Bohr radius, Energy Eigenvalues and Energy eigenfunctions in this dimensionless form.

   (f) Discuss the boundary conditions for numerical solution using finite difference method.

2. (10 marks) **Programming**

   (a) Write a Python code to

      i. Plot $V(r)$ and $V_{\text{eff}}(r)$ as a function of $r$ for $\ell = 1, 2, 3$ on the same plot. Take range of $r$ to be $[r_{\text{min}} : r_{\text{max}}]$ with $r_{\text{min}} = 10^{-14}$ and $r_{\text{max}} = 50$, $r$ being the dimensionless variable.

      ii. Determine the first ten energy eigenvalues and normalised eigenfunctions for $\ell = 0$ using finite difference method with $r_{\text{max}} = 10$.

      iii. plot the first four radial wavefunctions (as points) along with the corresponding analytical wavefunctions (as continuous curves).

   (b) Extend the code to determine the first ten energy eigenvalues and normalised eigenfunctions for $\ell = 1, 2$

   (c) Extend the code to plot all radial probability densities (as scatter plots) along with the corresponding analytical wavefunction (as continuous curves) for all $\ell$ corresponding to a given $n$. i.e. the following graphs

      i. radial probability density for $n = 1$, $\ell = 0$

      ii. radial probability density for $n = 2$, $\ell = 0$, 1

      iii. radial probability density for $n = 3$, $\ell = 0, 1$, 2

   (d) Repeat for $r_{\text{max}} = 2$, 20.