Assignment 9 - H-Atom Using Finite Difference Method

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Quantum Mechanics

Assignment 9 (H-Atom Using Finite Difference Method)

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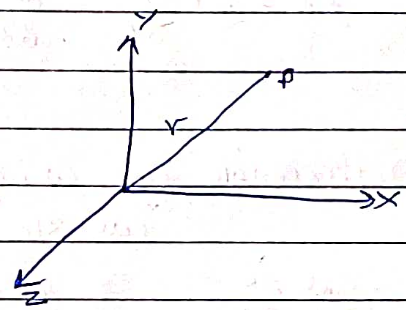
Theory

(a) Write Schrodinger Equation for an electron in H-atom potential in spherical coordinates.

Ans: The potential energy of a particle moving under central spherically symmetric field of force has the form $V(r)$ where r is distance b/w particle and centre of force. The schrodinger eqn for such system



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

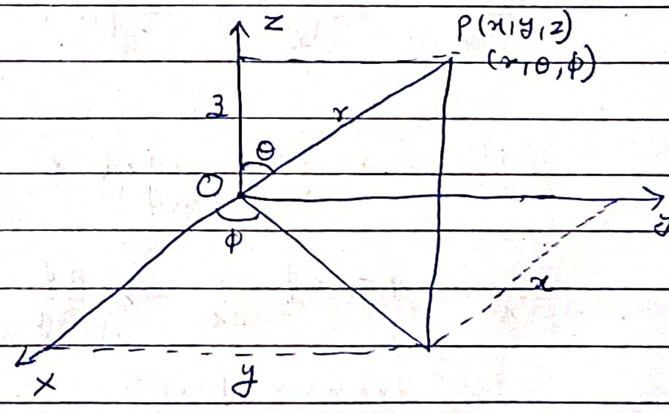
$$\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\psi + \frac{2m}{\hbar^2}[E-V(r)]\psi = 0 \quad -(1)$$

The relation between spherical & cartesian coordinate system is:

$x = r\sin\theta\cos\phi \quad -(2)$

$y = r\sin\theta\sin\phi \quad -(3)$

$z = r\cos\theta \quad -(4)$



(3)/(4) gives

$$\frac{y}{x} = \tan\phi \quad -(5)$$

From (4) $\cos\theta = z/r \quad -(6)$

square (2) (3) (4) & add

$$x^2+y^2+z^2 = r^2\sin^2\theta\cos^2\phi + r^2\sin^2\theta\sin^2\phi + r^2\cos^2\theta$$

$$= r^2\sin^2\theta(\cos^2\phi+\sin^2\phi) + r^2\cos^2\theta$$

$$\boxed{x^2+y^2+z^2 = r^2} \quad -(7)$$

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Let's take ψ in terms of polar coordinates $(r,\theta,\phi) \Rightarrow \psi(r,\theta,\phi)$

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

$$\frac{d\psi}{dx} = \frac{\partial \psi}{\partial r} \times \frac{\partial r}{\partial x} + \frac{\partial \psi}{\partial \theta} \times \frac{\partial \theta}{\partial x} + \frac{\partial \psi}{\partial \phi} \times \frac{\partial \phi}{\partial x} \quad (8)$$

Differentiate (7) w.r.t x

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

$$\cancel{2}x = \cancel{2}r\frac{dr}{dx} = \frac{dr}{dx} = \frac{x}{r} = \frac{\cancel{r}\sin\theta\cos\phi}{\cancel{r}} = \sin\theta\cos\phi \quad -(9)$$

Differentiate (6) w.r.t. x

$\downarrow$ $\cos\theta = z/r$

$$\cancel{-}\sin\theta\frac{\partial\theta}{\partial x} = \frac{-z}{r^2}\frac{\partial r}{\partial x} \Rightarrow \frac{-z}{r^2}\times\sin\theta\cos\phi = \frac{\cancel{-}\cancel{r}\cos\theta\,\cancel{\sin\theta}\cos\phi}{r^2}$$

$$\frac{\partial\theta}{\partial x} = \frac{\cos\theta\cos\phi}{r} \quad -(10)$$

Differentiate (5) w.r.t. x

$\downarrow$ $y/x = \tan\phi$

$$\frac{-y}{x^2} = +\sec^2\phi\frac{\partial\phi}{\partial x} \Rightarrow \frac{\partial\phi}{\partial x} = \frac{-y}{\sec^2\phi\times x^2} = \frac{-y\cos^2\phi}{x^2}$$

$$= \frac{-\cancel{r}\sin\theta\sin\phi\cancel{\cos^2\phi}}{r^{\cancel{2}}\sin^2\theta\cancel{\cos^2\phi}}$$

$$\frac{\partial\phi}{\partial x} = -\frac{\sin\phi}{r\sin\theta} \quad -(11)$$

Put (9), (10), (11) in (8)

$$\frac{\partial\psi}{\partial x} = \frac{\partial\psi}{\partial r}\times\sin\theta\cos\phi + \frac{\partial\psi}{\partial\theta}\times\frac{\cos\theta\cos\phi}{r} + \frac{\partial\psi}{\partial\phi}\frac{\sin\phi}{r\sin\theta} \quad -(12)$$

As we know we need $\frac{\partial^2\psi}{\partial x^2}$ in STISE

$$\frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\theta}{r\sin\theta}\frac{\partial}{\partial\phi} \quad -(13)$$

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$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial x}\right)$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\frac{\partial\psi}{\partial r}\times\frac{\partial r}{\partial x} + \frac{\partial}{\partial x}\frac{\partial\psi}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial}{\partial x}\frac{\partial\psi}{\partial\phi}\frac{\partial\phi}{\partial x}$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial r}\frac{\partial\psi}{\partial x}\frac{\partial r}{\partial x} + \frac{\partial}{\partial\theta}\frac{\partial\psi}{\partial x}\frac{\partial\theta}{\partial x} + \frac{\partial}{\partial\phi}\frac{\partial\psi}{\partial x}\frac{\partial\phi}{\partial x} \quad -(14)$$

Putting 9, 10, 11, 12 in (14) gives

$$\frac{d^2\psi}{\partial x^2} = \frac{\partial}{\partial r}\left[\sin\theta\cos\phi\frac{\partial\psi}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial\psi}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial\psi}{\partial\phi}\right]\sin\theta\cos\phi$$

$$+\frac{\partial}{\partial\theta}\left[\,----\,\right]\frac{\cos\theta\cos\phi}{r} + \frac{\partial}{\partial\phi}\left[\,----\,\right]\frac{-\sin\phi}{r\sin\theta} \quad -(15)$$

Similarly $\frac{\partial^2\psi}{\partial y^2}$ will come out to be

$$\frac{\partial\psi}{\partial y} = \sin\theta\sin\phi\frac{\partial\psi}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial\psi}{\partial\theta} + \frac{\cos\phi}{r\,\cancel{\cos}\sin\theta}\frac{\partial\psi}{\partial\phi} \quad (19)$$

$$\frac{\partial r}{\partial y} = \sin\theta\sin\phi \quad -(16)$$

$$\frac{\partial\theta}{\partial y} = \frac{\cos\theta\sin\phi}{r} \quad -(17)$$

$$\frac{\partial\phi}{\partial y} = \frac{\cos\phi}{r\,\cancel{\cos}\sin\theta} \quad -(18)$$

$$\frac{\partial^2\psi}{\partial y^2} = \frac{\partial}{\partial r}\left(\frac{\partial\psi}{\partial y}\right)\left(\frac{\partial r}{\partial y}\right) + \frac{\partial}{\partial\theta}\left(\frac{\partial\psi}{\partial y}\right)\left(\frac{\partial\theta}{\partial y}\right) + \frac{\partial}{\partial\phi}\left(\frac{\partial\psi}{\partial y}\right)\left(\frac{\partial\phi}{\partial y}\right) - (20)$$

Put 16, 17, 18, 19 in (20

$$\frac{\partial^2\psi}{\partial y^2} = \frac{\partial}{\partial r}\left[\sin\theta\sin\phi\frac{\partial\psi}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial\psi}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial\psi}{\partial\phi}\right]\sin\theta\sin\phi +$$

$$\frac{\partial}{\partial\theta}\left[\,---\,\right]\frac{\cos\theta\sin\phi}{r} + \frac{\partial}{\partial\phi}\left[\,---\,\right]\frac{\cos\phi}{r\sin\theta} \quad -(21)$$

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To find $\frac{\partial^2\psi}{\partial z^2}$, we've $\frac{\partial\psi}{\partial z} = \frac{\partial\psi}{\partial r}\frac{\partial r}{\partial z} + \frac{\partial\psi}{\partial\theta}\frac{\partial\theta}{\partial z} + \frac{\partial\psi}{\partial\phi}\frac{\partial\phi}{\partial z}$ -(25)

$\frac{\partial r}{\partial z} = \cos\theta$ -(22) $\qquad \frac{\partial\theta}{\partial z} = -\frac{\sin\theta}{r}$ -(23) $\qquad \frac{\partial\phi}{\partial z} = 0$ -(24)

Putting (22), (23), (24) in (25)

$$\frac{\partial\psi}{\partial z} = \cos\theta\frac{\partial\psi}{\partial r} - \frac{\sin\theta}{r}\frac{\partial\psi}{\partial\theta} \quad -(26)$$

Now, $\frac{\partial^2\psi}{\partial z^2} = \frac{\partial}{\partial r}\left(\frac{\partial\psi}{\partial z}\right)\left(\frac{\partial r}{\partial z}\right) + \frac{\partial}{\partial\theta}\left(\frac{\partial\psi}{\partial z}\right)\left(\frac{\partial\theta}{\partial z}\right) + \frac{\partial}{\partial\phi}\left(\frac{\partial\phi}{\partial z}\right)\left(\frac{\partial\phi}{\partial z}\right)$ -(27)

Putting 22, 23, 24, 26 in 27

$$\frac{\partial^2\psi}{\partial z^2} = \frac{\partial}{\partial r}\left[\cos\theta\frac{\partial\psi}{\partial r} - \frac{\sin\theta}{r}\frac{\partial\psi}{\partial\theta}\right]\cos\theta + \frac{\partial}{\partial\theta}\left[\cos\theta\frac{\partial\psi}{\partial r} - \frac{\sin\theta}{r}\frac{\partial\psi}{\partial\theta}\right]\left[-\frac{\sin\theta}{r}\right] \quad -(28)$$

Add (15), (21) & (28)

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} \quad (29)$$

Using (29) in

$$\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + \frac{2m}{\hbar^2}[E - V(r)]\psi \text{ is}$$

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

(b) Use separation of variable method to separate this into angular & radial part. (Use $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$ & take separation constant $l(l+1)$.

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S.E in polar form is given as:

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

Multiply both sides by $r^2\sin^2\theta$

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

Take $\psi(r,\theta,\phi)=R(r)P(\theta)Q(\phi)$ $-(2)$

Put (2) in (1)

$$\frac{1}{R(r)}\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{1}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P(\theta)}{\partial\theta}\right)\sin\theta+\frac{1}{Q(\phi)}\frac{\partial^2 Q(\phi)}{\partial\phi^2}+\frac{2m}{\hbar^2}(E-V)r^2\sin^2\theta=0$$

$$\frac{1}{R(r)}\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{1}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P(\theta)}{\partial\theta}\right)\sin\theta+\frac{2m(E-V)r^2\sin^2\theta}{\hbar^2}$$

$$=-\frac{1}{Q(\phi)}\frac{\partial^2 Q(\phi)}{\partial\phi^2}$$

LHS depends on r and θ whereas RHS depends on ϕ, but LHS=RHS, so they can be equated to a constant m^2

$$\frac{1}{R(r)}\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{1}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P(\theta)}{\partial\theta}\right)\sin\theta+\frac{2m(E-V)r^2\sin^2\theta}{\hbar^2}=m^2 \quad (3)$$

$$\frac{1}{R(r)}\cancel{\sin^2\theta}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{1}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P(\theta)}{\partial\theta}\right)\frac{1}{\sin\theta}+\frac{2m(E-V)r^2}{\hbar^2}=\frac{m^2}{\sin^2\theta}$$

Now again by separation of constant

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)-\frac{2m(E-V)r^2}{\hbar^2}=\frac{m^2}{\sin^2\theta}-\frac{1}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P(\theta)}{\partial\theta}\right)\frac{1}{\sin\theta} \quad (4)$$

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Equate (4) with a constant

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) - \frac{2m(E-V)r^2}{\hbar^2} = l(l+1)$$

Radial Part

$$\frac{m^2}{\sin^2\theta} - \frac{1}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial P(\theta)}{\partial\theta}\right)\frac{1}{\sin\theta} = l(l+1)$$

Angular Part

(C) Convert Radial Part into dimensionless form. Rescale r by G.R radius and energy with ground state energy

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) - \frac{2m(E-V)r^2}{\hbar^2} = l(l+1) \quad -(\cancel{2})$$

Taking $R = \frac{K}{r}$

$$\frac{dR}{dr} = \frac{\frac{dK}{dr}\times r - K}{r^2} \quad -(1)$$

$$\frac{\partial^2 R}{\partial r^2} = \frac{\partial K}{\partial r} \times \frac{1}{r} \quad -\frac{K}{r^2} \Rightarrow$$

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$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r}\right) = r^2 \frac{\partial^2 R}{\partial r^2} + 2r \times \frac{\partial R}{\partial r}$$

$$\downarrow$$

$$\frac{\partial}{\partial r}\left(\frac{\partial K}{\partial r} \times r - K\right) = \frac{\partial^2 K}{\partial r^2} \times r + \cancel{\frac{\partial K}{\partial r}} - \cancel{\frac{\partial K}{\partial r}} = \frac{\partial^2 K}{\partial r^2} \times r \quad -(2)$$

Using (2) in (1)

$$\frac{r}{K} \times \frac{\partial^2 K}{\partial r^2} \times r - \frac{2m(E-V)r^2}{\hbar^2} = l(l+1)$$

$$= \frac{r^2}{K} \frac{\partial^2 K}{\partial r^2} - \frac{2mr^2(E-V)}{\hbar^2} = l(l+1)$$

Multiply both sides with $\frac{-\hbar^2}{2mr^2}$

$$\frac{-\hbar^2}{2mr^2} \times \frac{\cancel{r^2}}{K} \frac{\partial^2 K}{\partial r^2} - (E-V) = l(l+1) \times \frac{-\hbar^2}{2mr^2}$$

$$-\frac{\hbar^2}{2mK} \frac{\partial^2 K}{\partial r^2} - (E-V)K = -l(l+1)\frac{\hbar^2}{2mr^2}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 K}{\partial r^2} \underbrace{\left(V + \frac{l(l+1)\hbar^2}{2mr^2}\right)}_{V_{effective}} K = EK \quad (3)$$

Now, Replace r_0 ~~by~~ r_0 which is bohr radius

As we know $r_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}$

Take $r' = \frac{r}{r_0}$

$$\frac{\partial r'}{\partial r} = \frac{1}{r_0}$$

$$\frac{\partial K}{\partial r} = \frac{\partial K}{\partial r'} \times \frac{\partial r'}{\partial r} \Rightarrow \frac{\partial K}{\partial r'} \times \frac{1}{r_0}$$

$$\frac{\partial^2 K}{\partial r^2} = \frac{\partial}{\partial r}\left(\frac{\partial K}{\partial r'}\right) = \frac{1}{r_0} \frac{\partial}{\partial r} \frac{\partial K}{\partial r'} = \frac{1}{r_0} \frac{\partial}{\partial r'} \frac{\partial K}{\partial r'} \times \frac{\partial r}{\partial r'} = \frac{1}{r_0^2} \frac{\partial^2 K}{\partial r'^2} \quad (4)$$

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From (3) Veffective is:

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

Taking $V(r)$ from classical theory

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

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

From $r' = r/r_0 \Rightarrow \boxed{r = r' r_0}$

$$V_{eff} = \frac{-e^2}{4\pi\varepsilon_0 \times r' r_0} + \frac{l(l+1)\hbar^2}{2m \times r'^2 r_0^2}$$

$$= \frac{-e^2 \times me^2}{4\pi\varepsilon_0 \times r' \times 4\pi\varepsilon_0 \hbar^2} + \frac{l(l+1)\hbar^2 \times m^2 e^4}{2m r'^2 \times 16\pi^2 \varepsilon_0^2 \hbar^4}$$

$$= \frac{-me^4}{16\pi^2\varepsilon_0^2 r' \hbar^2} + \frac{l(l+1)\hbar^2 m^2 e^4}{32 m \pi^2 \varepsilon_0^2 \hbar^4 r'^2}$$

$$V_{eff} = \frac{me^4}{16\pi^2\varepsilon_0^2\hbar^2}\left[\frac{-1}{r'} + \frac{l(l+1)}{2r'^2}\right] \quad -(5)$$

Put (4) & (5) in (3)

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r_0^2}\frac{\partial^2 k}{\partial r'^2}\left(\frac{me^4}{16\pi^2\varepsilon_0^2\hbar^2}\left(\frac{-1}{r'} + \frac{l(l+1)}{2r'^2}\right)\right)\right] = Ek$$

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$$\frac{-\hbar^2}{2m} \times \frac{1}{(4\pi\varepsilon_0)^2} \frac{m^2 e^4}{\hbar^4} \frac{d^2 K}{\partial r'^2} + \frac{me^4}{2(4\pi\varepsilon_0)^2 \hbar^2} \times 2\left[\frac{-1}{r'} + \frac{l(l+1)}{2r'^2}\right] = K(r').E$$

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

$$\frac{me^4}{2(4\pi\varepsilon_0)^2 \hbar^2}\left[\frac{-\partial^2 K}{\partial r'^2} + 2\left(\frac{-1}{r'} + \frac{l(l+1)}{2r'^2}\right)\right] = K(r')E$$

Ground State Energy of Hydrogen atom is

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

$$\left[\frac{-\partial^2 K}{\partial r'^2} + 2\left(\frac{-1}{r'} + \frac{l(l+1)}{2r'^2}\right)\right] = K(r') \frac{E}{\frac{me^4}{2(4\pi\varepsilon_0)^2 \hbar^2}}$$

Take $\frac{E}{E_1} = e$, which is dimensionless

$$\left[\frac{-\partial^2 K}{\partial r'^2} + 2\left(\frac{-1}{r'} + \frac{l(l+1)}{2r'^2}\right)\right] = K(r')\, e$$

This is radial Equation in Dimensionless form

(d) Discuss V_{eff} and it's implication---

Ans.

$$V_{eff} = \underbrace{\frac{-2}{r'}}_{\text{Coulombic/ Classical Potential}} + \underbrace{\frac{l(l+1)}{r'^2}}_{\text{Centrifugal force}}$$

Coulombic potential is attractive for opposite charges whereas Centrifugal term is always +ve
~~when~~ For first orbit $n=1$, $l=0$, In this case there is only coulombic potential affective. This is case of Hydrogen atom, where there is only one orbit which is very stable.

As l increases, impact of centrifugal term increases and V_{eff} reduces.

(e) Analytical Expression for Bohr Radius, Energy Eigen Values & Energy Eigen Functions:

Ans. 1. Bohr radius $(r_0) = \dfrac{4\pi\varepsilon_0\hbar^2}{me^2}$

Above we used Bohr radius to make r dimensionless.

2. Energy Eigen values:

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2}$$

$$E_n = \frac{-13.6}{n^2}$$

3 Energy Eigen States:

$$\psi_{nl} = 2\sqrt{\frac{(n-l-1)!}{n^4[(n+l)!]^3}}\, e^{-\xi}(2\xi)^l L_{n-l-1}^{2l+1}(2\xi)$$

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Q - Boundary Conditions for numerical solution using Finite Difference Method

Ans.

Radial wave function should be zero at $r=0$ and at $r=$ boundary point.

We don't use these boundary points in finite difference Matrix. The points which lie between boundary conditions approximated by finite difference method

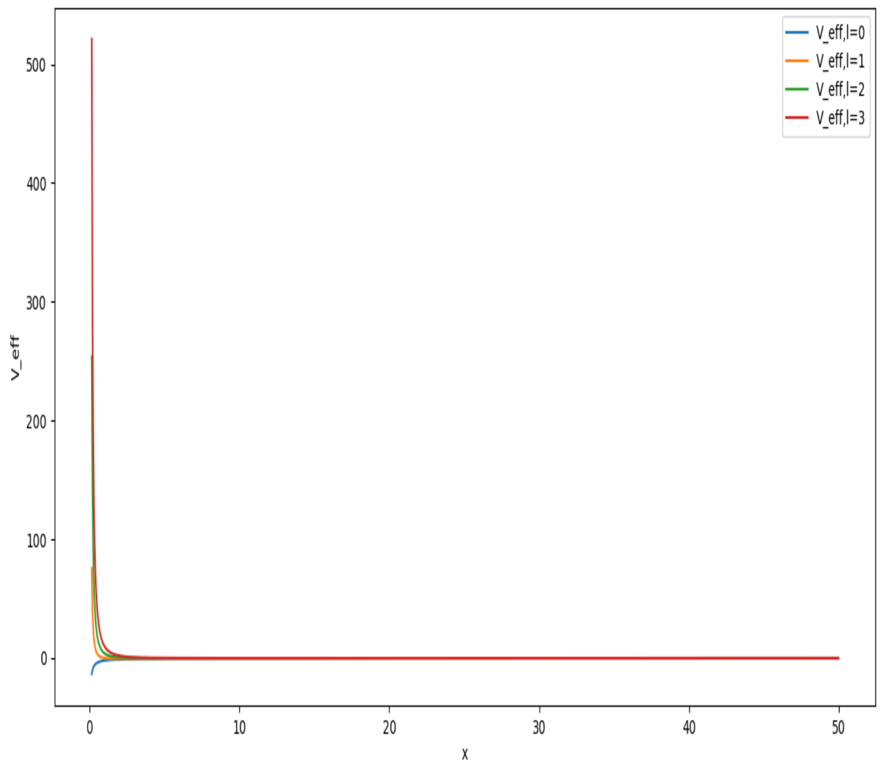
Programming

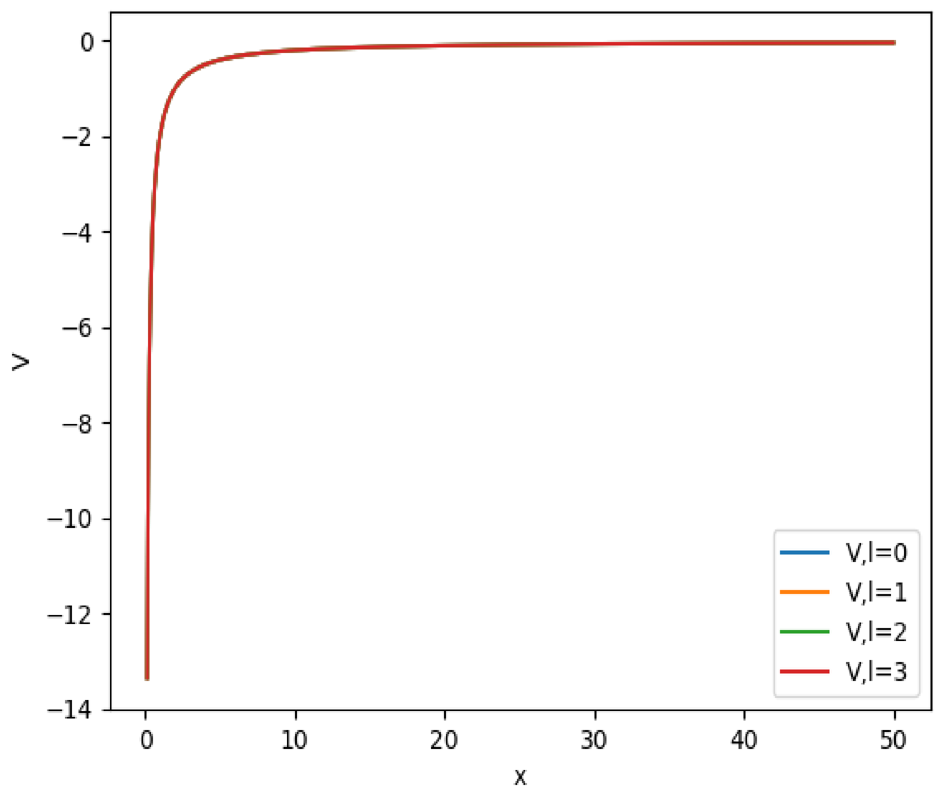
```python
import numpy as np
from scipy.linalg import eigh
import matplotlib.pyplot as plt
import scipy.integrate as integrate
import pandas as pd
from scipy.special import assoc_laguerre
def diag_mat(xi,xf,N,l):
    X = np.linspace(xi,xf,N+2)
    x=X[1:-1]
    h = x[1]-x[0]
    a,v=np.zeros((len(x),len(x))),np.zeros((len(x),len(x)))
    for i in range(len(x)):
        for j in range(len(x)):
            if i==j:
                a[i][i]=2/h**2
                v[i][i]=(-2/x[i])+((l)*(l+1))/(x[i]**2)
            elif i==j+1:
                a[i][j]=-1/h**2
            elif i == j-1:
                a[i][j] = -1/h**2
    A=(a+v)
    eig = eigh(A)
    return eig,x

def Analytic(x,n,l):
    return ((2*x/n)**(l)*assoc_laguerre(2*x/n,n-l-1,2*l+1))/(np.exp(x/n))*x

m=1.67*10**(-27)
def Veff(x, l):
    Vef = (l * (l + 1) / (x ** 2)) - (2 / x)
    V = - (2 / x)

    return Vef, V

def plot(i, l, power):
    H, x = diag_mat(0.01, 30, 1000, l)
    u = H[1][:, i]
    c = integrate.simps(u ** 2, x)
    N = u / np.sqrt(c)
    plt.plot(x, N ** power,label=f'l,n={l,i+1}')
    plt.title("Radial Probability Density for different n and l")
    plt.xlabel("x")
    plt.ylabel("$(u_r(\u03BE))^2$")
    plt.grid()
    plt.legend()

    # plt.show()

N=1000
xi=10**-14;xf=30

#A-i
# for i in range(0, 4):
#     H, x = diag_mat(0.1, 50, N, i)
#     Vef, V = Veff(x, i)
#     plt.scatter(x, V,label=f'V,l={i}')
#     # plt.plot(x, Vef,label=f'V_eff,l={i}')
#     plt.xlabel("x")
#     plt.ylabel("V_eff")
#     plt.legend()
# plt.show()

# for i in range(0, 4):
#     H, x = diag_mat(0.1, 50, N, i)
#     Vef, V = Veff(x, i)
```

```
#       plt.plot(x, V,label=f'V,l={i}')
#       plt.xlabel("x")
#       plt.ylabel("V")
#       plt.legend()
# plt.show()

#---------------------------------Q1_ii----------------------------------------#
for i in range(0,4,1):
    U_,x=diag_mat(xi,xf,N,0)
    U=U_[1][:,i]
    u_norm=U/np.sqrt(integrate.simps(np.power(U,2),x))
    U_anal = Analytic(x,i,0)
    u_anal_normalised=U_anal/np.sqrt(integrate.simps(np.power(U_anal,2),x))
    plt.scatter(x,np.power(u_norm,1),label=f'Numerical, n={i+1}')
    plt.plot(x,np.power(u_anal_normalised,1),label=f'Analytical, n={i+1}')
    plt.xlabel("x")
    plt.ylabel("$(u_r(\u03BE))$")
    plt.title("Radial Wavefunction for l=0")
plt.legend()
plt.show()

# #---------------------Q-a(ii)-------------------------#
# print("First 10 Energy Eigen Values for l=0 and r_max=30")
# p=[]
# for i in range(1,11):
#       p.append(-1/i**2)
# data ={
#       "Numerical Eigen Values ": U_[0][:10],
#       "Analytical Eigen Values ":p
# }
# print(pd.DataFrame(data))

# #---------------------------------Qb_i----------------------------------------#
# for i in range(0,4,1):
#       U_,x=diag_mat(xi,xf,N,1)
#       U=U_[1][:,i]
#       u_norm=U/np.sqrt(integrate.simps(np.power(U,2),x))
#       U_anal = Analytic(x,i,1)
#       u_anal_normalised=U_anal/np.sqrt(integrate.simps(np.power(U_anal,2),x))
#       plt.scatter(x,np.power(u_norm,1),label=f'Numerical, n={i+1}')
#       plt.plot(x,np.power(u_anal_normalised,1),label=f'Analytical, n={i+1}')
# plt.legend()
# plt.show()

# print("First 10 Energy Eigen Values for l=1 and r_max=30")
# p=[]
# for i in range(1,11):
#       p.append(-1/(i+1)**2)
# data ={
#       "Numerical Eigen Values ": U_[0][:10],
#       "Analytical Eigen Values ":p
# }
# print(pd.DataFrame(data))

#---------------------------------Qb_i----------------------------------------#
# for i in range(0,4,1):
#       U_,x=diag_mat(xi,xf,N,2)
#       U=U_[1][:,i]
#       u_norm=U/np.sqrt(integrate.simps(np.power(U,2),x))
#       U_anal = Analytic(x,i,2)
#       u_anal_normalised=U_anal/np.sqrt(integrate.simps(np.power(U_anal,2),x))
#       plt.scatter(x,np.power(u_norm,1),label=f'Numerical, n={i+1}')
#       plt.plot(x,np.power(u_anal_normalised,1),label=f'Analytical, n={i+1}')
# plt.legend()
# plt.show()

# print("First 10 Energy Eigen Values for l=2 and r_max=30")
```

```
# p=[]
# for i in range(1,11):
#     p.append(-1/(i+2)**2)
# data ={
#     "Numerical Eigen Values ": U_[0][:10],
#     "Analytical Eigen Values ":p
# }
# print(pd.DataFrame(data))

# C

# '''for n=1:'''
# plot(0, 0, 2)
# plt.show()
# '''for n=2:'''
# plot(1, 0, 2)
# plot(1, 1, 2)
# plt.show()
#n=3
# plot(2, 0, 2)
# plot(2, 1, 2)
# plot(2, 2, 2)
# plt.show()
```

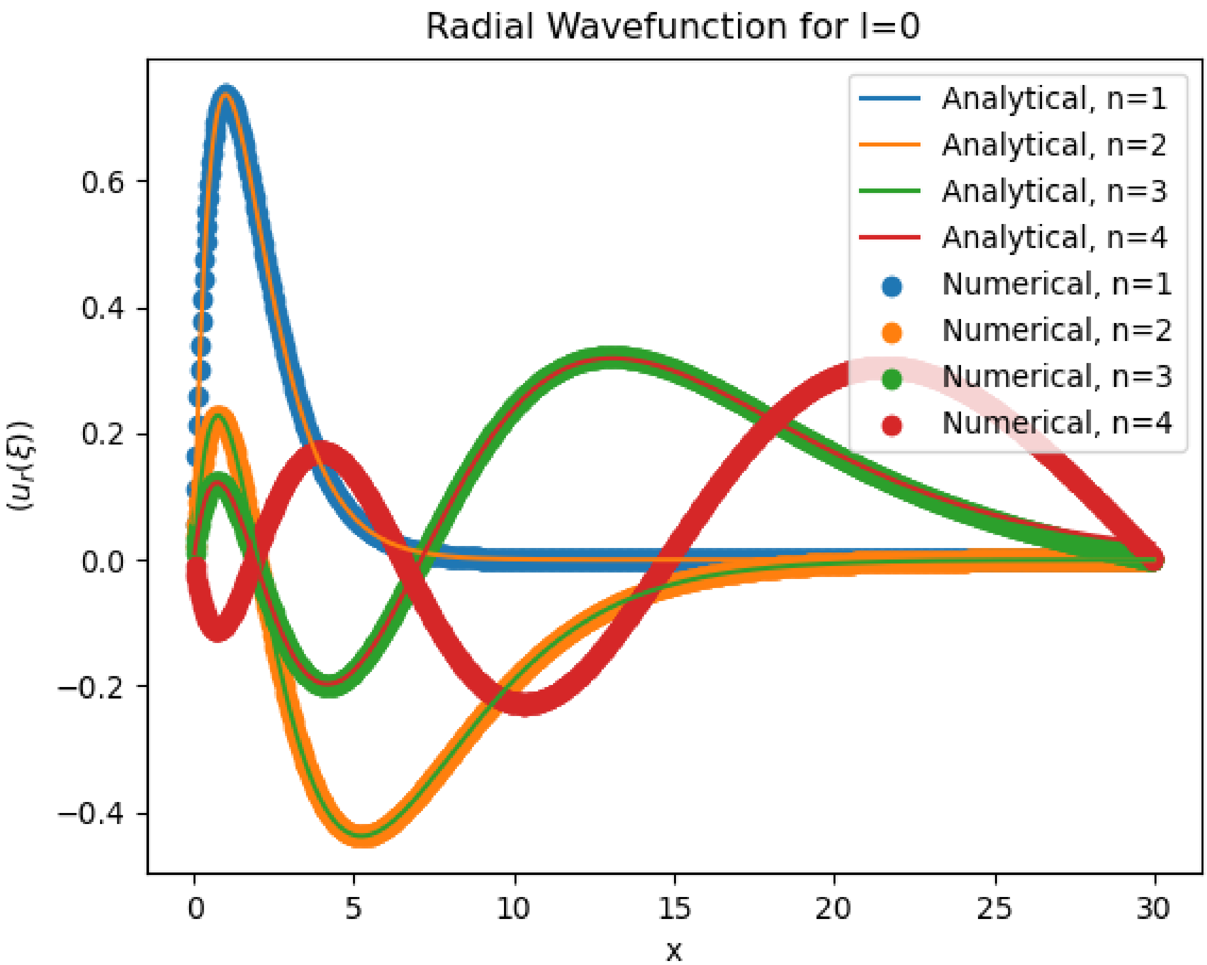
Result and Discussion




0
−2
−4
−6
−8
−10
−12
−14
V
0
10
20
30
40
50
x
V,l=0
V,l=1
V,l=2
V,l=3

```
First 10 Energy Eigen Values for l=0 and r_max=30
```

	Numerical Eigen Values	Analytical Eigen Values
0	-0.994448	-1.000000
1	-0.249650	-0.250000
2	-0.111042	-0.111111
3	-0.062478	-0.062500
4	-0.039991	-0.040000
5	-0.027773	-0.027778
6	-0.020404	-0.020408
7	-0.015486	-0.015625
8	-0.010951	-0.012346
9	-0.005294	-0.010000

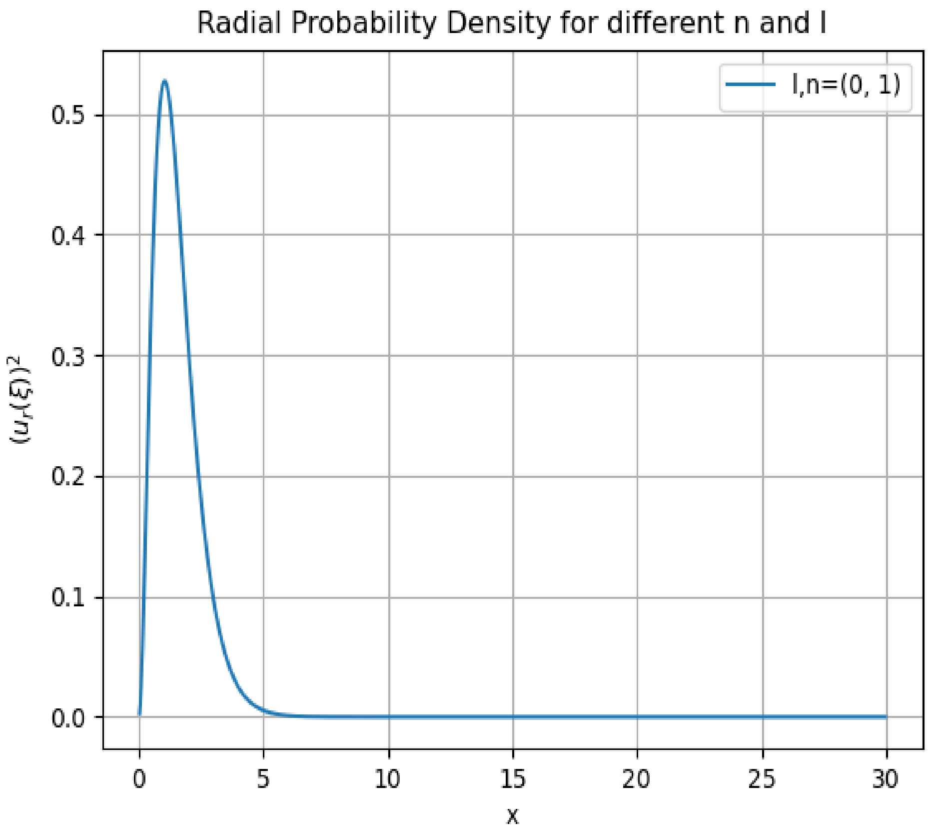

Radial Wavefunction for l=0
Analytical, n=1
Analytical, n=2
Analytical, n=3
Analytical, n=4
Numerical, n=1
Numerical, n=2
Numerical, n=3
Numerical, n=4
0.6
0.4
0.2
0.0
−0.2
−0.4
$\langle u_r(\xi)\rangle$
0
5
10
15
20
25
30
x

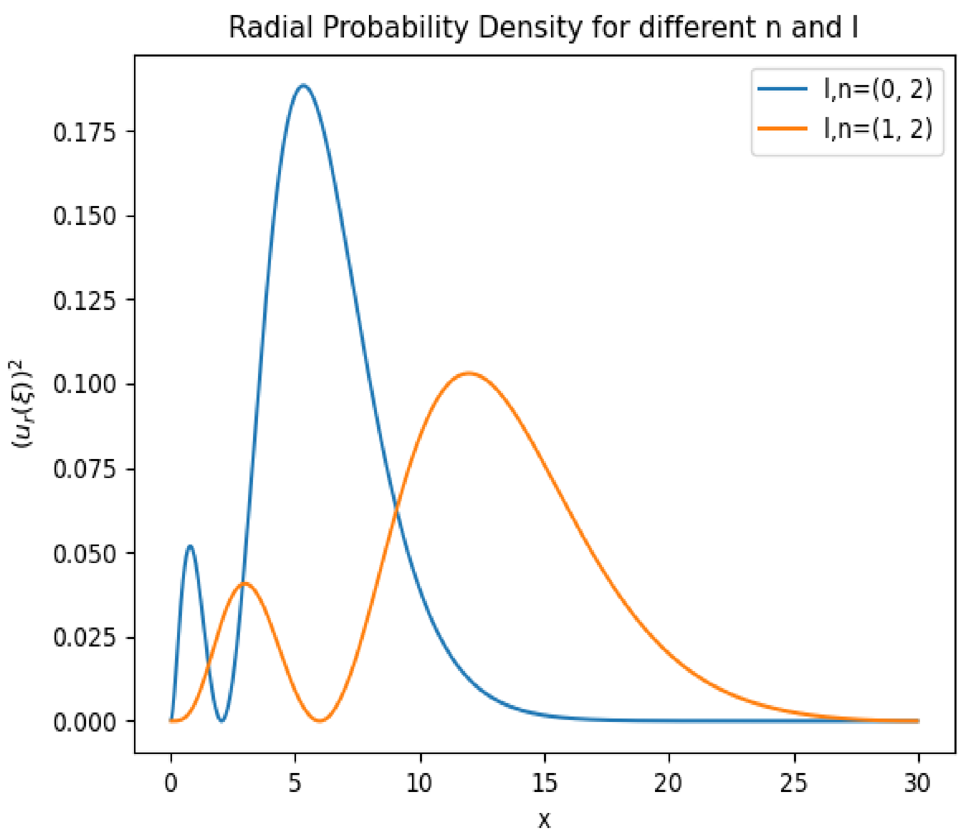
First 10 Energy Eigen Values for l=1 and r_max=30

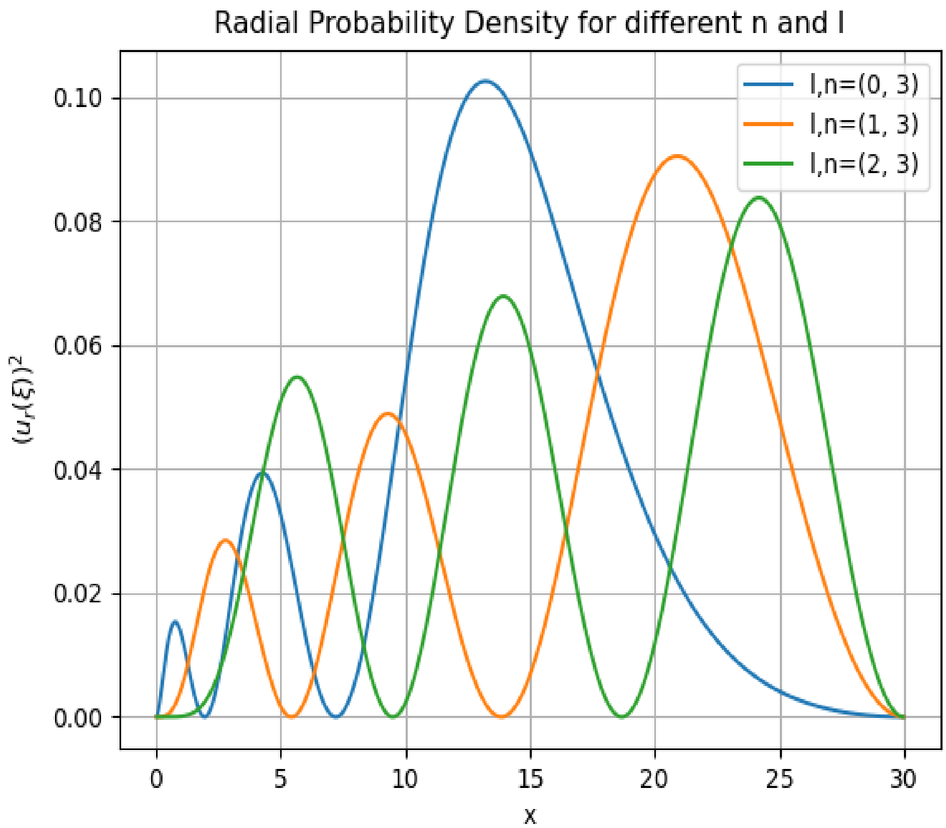
	Numerical Eigen Values	Analytical Eigen Values
0	-0.250117	-0.250000
1	-0.111165	-0.111111
2	-0.062528	-0.062500
3	-0.040016	-0.040000
4	-0.027788	-0.027778
5	-0.020413	-0.020408
6	-0.015506	-0.015625
7	-0.011037	-0.012346
8	-0.005481	-0.010000
9	0.001326	-0.008264

First 10 Energy Eigen Values for l=2 and r_max=30

	Numerical Eigen Values	Analytical Eigen Values
0	-0.111116	-0.111111
1	-0.062504	-0.062500
2	-0.040003	-0.040000
3	-0.027780	-0.027778
4	-0.020409	-0.020408
5	-0.015526	-0.015625
6	-0.011183	-0.012346
7	-0.005818	-0.010000
8	0.000775	-0.008264
9	0.008496	-0.006944


Radial Probability Density for different n and l
l,n=(0, 1)
$(u_r(\xi))^2$
0.0
0.1
0.2
0.3
0.4
0.5
0
5
10
15
20
25
30
x


Radial Probability Density for different n and l
l,n=(0, 2)
l,n=(1, 2)
0.175
0.150
0.125
0.100
0.075
0.050
0.025
0.000
$(u_r(\xi))^2$
0
5
10
15
20
25
30
x


Radial Probability Density for different n and l
l,n=(0, 3)
l,n=(1, 3)
l,n=(2, 3)
0.10
0.08
0.06
0.04
0.02
0.00
$(u_r(\xi))^2$
0
5
10
15
20
25
30
x