Quantum Mechanics and its Applications (PHY-RC-5016)
Fifth semester Physics Honours

Kishore Dutta
Department of Physics, Handique Girls' College

August 6, 2024

1 Radial Solution of Hydrogen Atom Problem

The Schrödinger equation for the hydrogen atom problem can be expressed as

$$\nabla^2\psi + \frac{2\mu}{\hbar^2}\left(E + \frac{ze^2}{r}\right)\psi = 0,$$

where $\mu = \frac{m_1 m_2}{m_1+m_2}$ is the reduced mass of the nucleus and the electron of the hydrogen atom. In spherical polar coordinate, the above equation can be written as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial r^2} + \frac{2\mu}{\hbar^2}\left(E + \frac{ze^2}{r}\right)\psi = 0.$$

This equation can be solved using separation of variable technique. Writing

$$\psi = \psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi),$$

the above equation can be expressed as

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\phi^2} + \frac{2\mu r^2}{\hbar^2}\left(E + \frac{ze^2}{r}\right) = 0. \tag{1}$$

Multiplying on both sides by $\sin^2\theta$, we have

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{2\mu}{\hbar^2}\left(E + \frac{ze^2}{r}\right)r^2\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}.$$

This equation can be correct only if both sides of it are equal to the same constant, since they are functions of different variables. Thus, the differential equation for ϕ can be written as

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m_\ell^2, \tag{2}$$

so that

$$\frac{d^2\Phi}{d\phi^2} + m_\ell^2\Phi = 0 \quad \Rightarrow \quad \Phi(\phi) = Ae^{im_\ell\phi}.$$

Since $\Phi(\phi) = \Phi(\phi + 2\pi)$ (same meridian plane), we have $Ae^{im_\ell\phi} = Ae^{im_\ell(\phi+2\pi)}$, which can only happen when m_ℓ is 0 or a positive or negative integer ($\pm1, \pm2, \pm3, \cdots$). The constant m_ℓ is known as magnetic quantum number of the hydrogen atom.

Now, Eq. (1) can be written as

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{2\mu r^2}{\hbar^2}\left(E + \frac{ze^2}{r}\right) = \frac{m_\ell^2}{\sin^2\theta}.$$

Rearranging r and θ dependent parts, we have

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(E + \frac{ze^2}{r}\right) = \frac{m_\ell^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right).$$

Thus, we have again arrived at an equation where different variables appear on each side, requiring that both sides be equal to the same constant. This constant we shall call $\ell(\ell+1)$. The equation for the functions R and Θ are, therefore, given by

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(E + \frac{ze^2}{r}\right) = \ell(\ell+1) \tag{3}$$

$$\frac{m_\ell^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = \ell(\ell+1). \tag{4}$$

The solution of the differential equation for the radial part $R(r)$ of the hydrogen atom wave function ψ is complicated, being in terms of polynomial called the associated Leguerre function. Eq. (3) can be solved only when E is positive or has one of the negative values E_n (signifying that the electron is bound to the atom) specified by

$$E_n = -\frac{\mu z^2 e^4}{2\hbar^2 n^2}, \quad n = 1, 2, 3, \ldots$$

This can be expressed as

$$E_n = -\frac{\mu z^2 e^4}{2\hbar^2}\left(\frac{1}{n^2}\right), \tag{5}$$

the same formula for the energy levels of the hydrogen atom that Bohr obtained.

2 Solution of Radial Equation

Let us consider the bound state problem ($E < 0$). Eq. (3) can be written as

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2\mu}{\hbar^2}\left(E + \frac{ze^2}{r} - \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right)R = 0 \tag{6}$$

This gives

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\left(\frac{2\mu E}{\hbar^2}+\frac{2\mu ze^2}{\hbar^2 r}-\frac{\ell(\ell+1)}{r^2}\right)R=0 \tag{7}$$

Below let's discuss separately the methods of finding the solution of the above equation by theoretical and numerical techniques.

2.1 Theoretical method

Let us introduce the new variables

$$\alpha=-\left(\frac{8\mu E}{\hbar^2}\right)^{1/2}, \qquad \lambda=\frac{2\mu ze^2}{\alpha\hbar^2}=\frac{ze^2}{\hbar}\left(-\frac{\mu}{2E}\right)^{1/2}.$$

Writing $\rho=\alpha r$ and dividing Eq. (7) throughout by α^2, we can write it in dimensionless form as

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{d\mathcal{R}}{d\rho}\right)+\left[\frac{\lambda}{\rho}-\frac{1}{4}-\frac{\ell(\ell+1)}{\rho^2}\right]\mathcal{R}=0, \tag{8}$$

where $\mathcal{R}(\rho)=R(r)$.

In the asymptotic limit, i.e, in the $\rho\to\infty$ limit, the term $-1/4$ is dominant within the square brackets. In that case, the above equation becomes

$$\frac{d^2\mathcal{R}}{d\rho^2}-\frac{1}{4}\mathcal{R}=0,$$

whose physically acceptable solution becomes $\mathcal{R}(\rho)\sim e^{-\rho/2}$. Thus we can write $\mathcal{R}(\rho)=K(\rho)e^{-\rho/2}$, where $K(\rho)$ is an unknown function. Further, since $\mathcal{R}(\rho)\sim\rho^\ell$ in small ρ limit, we can write

$$\mathcal{R}(\rho)=\rho^\ell e^{-\rho/2}L(\rho). \tag{9}$$

Substituting Eq. (9) into Eq. (8), we have a differential equation for $L(\rho)$, given by

$$\rho\frac{d^2L}{d\rho^2}+[2(\ell+1)-\rho]\frac{dL}{d\rho}+[\lambda-(\ell+1)]L=0. \tag{10}$$

To solve this equation, let's assume a solution for $L(\rho)$ in the series form:

$$L(\rho)=c_0+c_1\rho+c_2\rho^2+\cdots=\sum_{s=0}^{\infty}c_s\rho^s.$$

Since we know that $\mathcal{R}(\rho)$ behaves like ρ^ℓ for small ρ, $L(\rho)$ must tend to a constant as $\rho\to 0$. This is why the series has been taken to start with a constant term. This gives a recursion relation

$$c_{s+1}=\frac{s+\ell+1-\lambda}{(s+1)(s+2\ell+2)}c_s. \tag{11}$$

This shows that, for large s,

$$\frac{c_{s+1}}{c_s} \to \frac{1}{s},$$

which is just the ratio of successive coefficients in the expression of e^{ρ}. Thus, if the series for $L(\rho)$ does not terminate, then $L(\rho) \to \text{constant}.e^{\rho}$ for $\rho \to \infty$, giving a divergent behavior for $\mathcal{R}(\rho)$: $\mathcal{R}(\rho) \to \text{constant}.\rho^{l} e^{\rho/2}$. To avoid this, we have to make the series terminate. This can be done by choosing

$$\lambda = n = \text{integer},$$

so that when s reaches the value n' given by

$$n' = n - \ell - 1 \tag{12}$$

the factor $(s + \ell + 1 - \lambda)$ vanishes. Consequently, c'_{n+1} and all higher coefficients become zero, and $L(\rho)$ becomes a polynomial. The degree of the polynomial n' must, of course, be a non-negative integer. Hence it follws from Eq. (12) that the possible values of $n = n' + \ell + 1$ are the positive integers, and that ℓ cannot exceed $(n - 1)$, i.e.,

$$\ell = 0, 1, 2, \ldots, (n - 1).$$

Thus we may tabulate the three quantum numbers n, ℓ and m_ℓ together with their possible values as follows:

$$\begin{aligned} &n = 1, 2, 3, \ldots \quad \text{principal quantum number} \\ &\ell = 0, 1, 2, \ldots, (n-1) \quad \text{orbital quantum number} \\ &m_\ell = 0, \pm 1, \pm 2, \ldots, \pm \ell \quad \text{magnetic quantum number} \end{aligned} \tag{13}$$

Substituting $\lambda = n$, we have

$$E_n = -\frac{\mu z^2 e^4}{2\hbar^2}\left(\frac{1}{n^2}\right).$$

The total energy can be expressed as the sum of kinetic (T) and potential (V) energy:

$$E = T + V = T_{\text{radial}} + T_{\text{orbital}} - \frac{ze^2}{r}.$$

Thus, Eq. (3) can be exrpressed as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left(T_{\text{radial}} + T_{\text{orbital}} - \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}\right) R = 0.$$

If the last two terms in the square brackets of this equation cancel each other, we shall have a differential equation for $R(r)$ that involves functon of the radial vector $\mathbf{r}$ exclusively. We therefore require that

$$T_{\text{orbital}} = \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \quad \Rightarrow \quad \frac{1}{2}\mu v^2_{\text{orbital}} = \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}.$$

Writting the angular momentum $L = \mu v_{\text{orbital}} r$, we have

$$\frac{L^2}{2\mu r^2} = \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2},$$

giving

$$L = \sqrt{\ell(\ell+1)}\ \hbar.$$

It is customary to express the polynomial solution of Eq. (10) for $\lambda = n = 1, 2, \cdots$ in terms of the associated Laguerre polynomials $L_q^p(\rho)$. The Laguerre polynomials are given by

$$L_q(\rho) = e^{\rho}\frac{d^q}{d\rho^q}(e^{-\rho}\rho^q) = \left(e^{\rho}\frac{d}{d\rho}e^{-\rho}\right)^q \rho^q.$$

The associate Laguerre polynomials are given by

$$L_q^p(\rho) = \frac{d^p}{d\rho^p}L_q(\rho) = \frac{q!}{(q-p)!}(-\rho^{-p})e^{\rho}\frac{d^q}{d\rho^q}\left(e^{-\rho}\rho^{q-p}\right) = \frac{q!}{(q-p)!}e^{\rho}\frac{d^q}{d\rho^q}\left(e^{-\rho}\rho^{q-p}\right).$$

They may be defined through the generating function as

$$G^p(\rho,\xi) = \sum_{q=p}^{\infty}\frac{L_q^p(\rho)\xi^q}{q!} = \left(-\frac{\xi}{1-\xi}\right)^p \frac{e^{-\rho\xi(1-\xi)}}{1-\xi}$$

and satisfy the differential equation

$$\rho\frac{d^2L_q^p}{d\rho^2} + (p+1-\rho)\frac{dL_q^p}{d\rho} + qL_q^p = 0.$$

This equation can be compared with the Eq. (10) for $\lambda = n$, giving $p = 2\ell + 1$ and $q = n - \ell - 1$. Thus the polynomial solution is the associated Laguerre polynomials $L_{n-\ell-1}^{2\ell+1}(\rho)$ apart from an arbitrary constant factor $\mathcal{N}_{n\ell}$. Correspondingly, $\mathcal{R}(\rho)$ for a given n and ℓ is obtained from Eq. (9) as

$$\mathcal{R}_{n\ell}(\rho) = \mathcal{N}_{n\ell}\rho^{\ell}e^{-\rho/2}L_{n-\ell-1}^{2\ell+1}(\rho), \tag{14}$$

where $\rho = \alpha r = \frac{2zr}{na}$ with $a = \frac{\hbar^2}{\mu e^2}$ the Bohr radius. In terms of r, the radial solution for $z = a$ can simply be expressed as

$$R_{nl}(r) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!)^3]}}e^{-r/na}\left(\frac{2r}{na}\right)^{\ell}\cdot L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na}\right). \tag{15}$$

Table 1 shows some radial wave functions of hydrogen-like atoms for different orbitals.

Table 1: The radial wave function $\mathcal{R}_{n\ell}(r)$ for the hydrogen-like atom

n	ℓ	Spectroscopic notation	$R_{n\ell}(r)$
1	0	1s	$2\left(\frac{z}{a}\right)^{3/2} e^{-zr/a}$
2	0	2s	$\frac{1}{\sqrt{2}}\left(\frac{z}{a}\right)^{3/2}\left(1-\frac{zr}{2a}\right)e^{-zr/2a}$
2	1	2p	$\frac{1}{\sqrt{24}}\left(\frac{z}{a}\right)^{5/2} e^{-zr/2a}$
3	0	3s	$\frac{2}{3\sqrt{3}}\left(\frac{z}{a}\right)^{3/2}\left(1-\frac{2zr}{3a}+\frac{2z^2r^2}{27a^2}\right)e^{-zr/3a}$
3	1	3p	$\frac{4}{27}\sqrt{\frac{2}{3}}\left(\frac{z}{a}\right)^{5/2} r\left(1-\frac{zr}{6a}\right)e^{-zr/3a}$
3	2	3d	$\frac{4}{81}\frac{1}{\sqrt{30}}\left(\frac{z}{a}\right)^{7/2} r^2 e^{-zr/3a}$

2.2 Different Numerical method of solving radial equation

2.2.1 Using Laguerre polynomial as a special function

Using the Laguerre polynomial, we can only plot the Eigen functions given by Eq. (15). The python code and the output are displayed below:

```
import numpy as np
import matplotlib.pyplot as plt
from matplotlib import cm, colors
import scipy.integrate as integrate
import scipy.special as spe
def psi_R(r,n,l):
    coeff = np.sqrt((2.0/n)**3 * spe.factorial(n-l-1) /(2.0*n*spe.factorial
                                            (n+l)**3))
    laguerre = spe.assoc_laguerre(2.0*r/n,n-l-1,2*l+1)
    return coeff * np.exp(-r/n) * (2.0*r/n)**l * laguerre
r = np.linspace(0,10,1000)

R = psi_R(r,n=1,l=0)
plt.plot(r, R, lw=3, color=’b’, label=’$R_{nl}(r)$’)
plt.plot(r, R**2, lw=3, color=’r’, label=’$R_{nl}^2(r)$’)
plt.legend()
plt.xlabel(’$r (units: a_0)$’,fontsize=20)
plt.ylabel(’$R_{nl}(r), R_{nl}^2(r)$’, fontsize=20)
plt.title("Hydrogen Atom, $n=1$, $l = 0$ states")
plt.show()
```

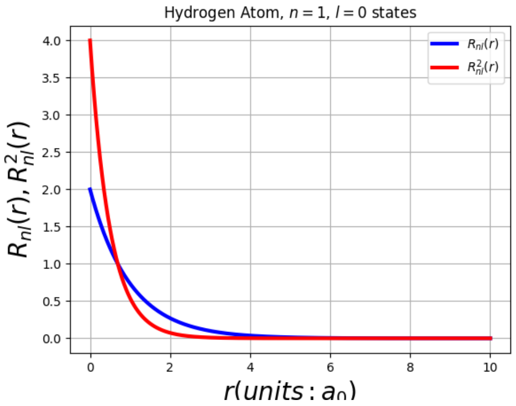


Figure 1: Plot of eigenfunction using Laguerre polynomial

2.2.2 Finite difference method

The numerical technique that we shall discuss here is the *Finite Difference Discretisation*. Being an efficient approach to solve differential equations numerically, the finite difference method approximates the differential operator by simple differences. The derivative is simply defined in the form of a limit, given by

$$\frac{df(x)}{dx} = \lim_{\Delta \to 0} \left[\frac{f(x+\Delta) - f(x)}{\Delta} \right],$$

where the domain of the function is discretised with some finite but infinitesimal step h. In fact, this expression for first order derivative comes from the Taylor's expansion of $f(x)$ about h, which could be expressed as

$$f(x+h) = f(x) + hf'(x) + \frac{h^2}{2!} f''(x) + \ldots.$$

Similarly, we can obtain

$$f(x-h) = f(x) - hf'(x) + \frac{h^2}{2!} f''(x) + \ldots.$$

These two expressions give

$$f(x+h) + f(x-h) = 2f(x) + h^2 f''(x) + \ldots$$

Thus,

$$f''(x) \approx \frac{f(x-h) - 2f(x) + f(x+h)}{h^2}$$

For numerical computation, instead of h we are using Δ. To define the second derivative, we need to take into account at least three points in the discretised domain. These three points can be $x - \Delta$, x, and $x + \Delta$. Thus we can define

$$\frac{d^2 f(x)}{dx^2} \approx \lim_{\Delta \to 0} \frac{\frac{f(x+\Delta)-f(x)}{\Delta} - \frac{f(x)-f(x-\Delta)}{\Delta}}{\Delta} = \lim_{\Delta \to 0} \frac{f(x-\Delta) - 2f(x) + f(x+\Delta)}{\Delta^2}.$$

This idea of numerical technique can now be applied to solve Schrödinger equations.

As a simple example, let's consider the problem of a particle in a box the Schrödinger equation of which can be written as

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x).$$

To solve it numerically, we need to discretise the domain (the bottom of the infinitely deep potential well) using a regular step of size h. The desired solution is the list of values $\psi(0),\ \psi(\Delta),\ \psi(2\Delta),\ \ldots,\ \psi((N+1)\Delta)$, which we can index using an integer i. For each of these values, we can write down an equation of the form:

$$\frac{d^2\psi_i}{dx^2} = -\frac{2mE}{\hbar^2}\psi_i, \quad \forall\ i \in \{1, 2, \ldots, N\},$$

where $N + 2$ is the total number of points in the discretised domain. Now with the help of the approximation for the second derivative, we can write

$$\frac{\psi_{i-1} - 2\psi_i + \psi_{i+1}}{\Delta^2} = -\frac{2mE}{\hbar^2}\psi_i, \quad \forall i \in \{1, 2, \ldots, N\}$$

This system of equations can be expressed in a concise form as a single matrix equation, given by

$$\begin{pmatrix} -2 & 1 & & & \\ 1 & -2 & 1 & & \\ & 1 & -2 & \ddots & \\ & & \ddots & \ddots & 1 \\ & & \ddots & 1 & -2 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \\ \psi_N \end{pmatrix} = -\frac{2mE}{\hbar^2} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \\ \psi_N \end{pmatrix}.$$

This is nothing but an eigenvalue problem solution of which gives set of eigenvalues $\frac{2mE}{\hbar^2}$ (representing the energy levels) and a corresponding set of eigenvectors ψ (representing the solution).

We can now apply the above-mentioned finite difference scheme to the radial equation of the hydrogen problem. The radial equation that we have displayed in Eq. (7) can be expressed as

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} + E\right) R = 0. \tag{16}$$

Let's define $\rho = r\ R$ so that we can write the differential operator as

$$\frac{d}{dr}\left(r^2\frac{d}{dr}\frac{\rho}{r}\right) = \frac{d}{dr}\left(r\frac{d\rho}{dr}\right) - \rho = r\frac{d^2\rho}{dr^2} + \frac{d\rho}{dr} - \frac{d\rho}{dr} = r\frac{d^2\rho}{dr^2}.$$

Thus Eq. (16) can be expressed as

$$r\frac{d^2\rho}{dr^2} - \frac{2\mu r^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} + E\right)\frac{\rho}{r} = 0,$$

giving

$$\frac{d^2\rho}{dr^2} + \frac{2\mu}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} + E\right)\rho = 0.$$

This can also be expressed as

$$-\frac{\hbar^2}{2\mu}\frac{d^2\rho}{dr^2} - \frac{e^2}{4\pi\epsilon_0 r}\rho + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}\rho = E\rho. \tag{17}$$

Eq. (17) is an eigenvalue equation, $H\rho = E\rho$, with

$$H \equiv -\frac{\hbar^2}{2\mu}\left(\frac{d^2}{d\rho^2} - \frac{\ell(\ell+1)}{r^2}\right) - \frac{e^2}{4\pi\epsilon_0 r},$$

where the first term is the Laplace term, second term is the angular term and the last term is the potential term.

We can now discretise the radial coordinate using an equidistant grid r_i comprising N elements with a displacement of $\Delta \equiv r_{i+1} - r_i$. The discretised Hamiltonian now consists of three terms: the first corresponds to the Laplace operator which can be expressed as a tridiagonal matrix:

$$-\frac{\hbar^2}{2\mu}\begin{pmatrix} -2 & 1 & & & \\ 1 & -2 & 1 & & \\ & 1 & -2 & \ddots & \\ & & \ddots & \ddots & 1 \\ & & & 1 & -2 \end{pmatrix}$$

The other two terms result in diagonal matrices:

$$\frac{\hbar^2\ell(\ell+1)}{2\mu}\begin{pmatrix} \frac{1}{r_1^2} & & & \\ & \frac{1}{r_2^2} & & \\ & & \ddots & \\ & & & \frac{1}{r_N^2} \end{pmatrix} \quad \text{and} \quad -\frac{e^2}{4\pi\epsilon_0}\begin{pmatrix} \frac{1}{r_1} & & & \\ & \frac{1}{r_2} & & \\ & & \ddots & \\ & & & \frac{1}{r_N} \end{pmatrix}$$

Below we provide the python codes for finding the probability density for different values of ℓ.

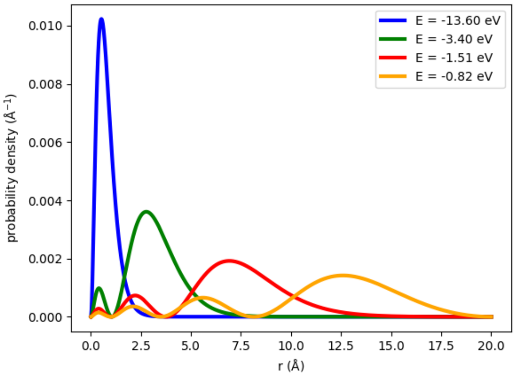


Figure 2: Plot of eigenvalues and eigenfunctions using finite difference method

```
import numpy as np
from scipy import constants as const
from scipy import sparse as sparse
from scipy.sparse.linalg import eigs
from matplotlib import pyplot as plt

hbar = const.hbar
e = const.e
m_e = const.m_e
pi = const.pi
epsilon_0 = const.epsilon_0
joul_to_eV = e

def calculate_laplace_three_point(r):
    h = r[1] - r[0]
    main_diag = -2.0 / h**2 * np.ones(N)
    off_diag  =  1.0 / h**2 * np.ones(N - 1)
    laplace_term = sparse.diags([main_diag, off_diag, off_diag],(0, -1, 1))
    return laplace_term

def calculate_angular_term(r):
    angular = l * (l + 1) / r**2
    angular_term = sparse.diags((angular))
    return angular_term

def calculate_potential_term(r):
    potential = e**2 / (4.0 * pi * epsilon_0) / r
    potential_term = sparse.diags((potential))
```

```
    return potential_term

def build_hamiltonian(r):
    laplace_term =   calculate_laplace_three_point(r)
    angular_term =   calculate_angular_term(r)
    potential_term = calculate_potential_term(r)
    hamiltonian = -hbar**2 /(2.0 * m_e)*(laplace_term-angular_term)-
                                         potential_term
    return hamiltonian

N = 2000
l = 0
r = np.linspace(2e-9, 0.0, N, endpoint=False)
hamiltonian = build_hamiltonian(r)
’’’ solve eigenproblem ’’’
number_of_eigenvalues = 30
eigenvalues, eigenvectors = eigs(hamiltonian, k=number_of_eigenvalues,
                                     which=’SM’)
 ’’’ sort eigenvalue and eigenvectors ’’’
eigenvectors = np.array([x for _, x in sorted(zip(eigenvalues, eigenvectors
                                     .T), key=lambda pair: pair[0])])
eigenvalues = np.sort(eigenvalues)

’’’compute probability density for each eigenvector ’’’
densities = [np.absolute(eigenvectors[i, :])**2 for i in range(len(
                                     eigenvalues))]
def plot(r, densities, eigenvalues):
    plt.xlabel(’r ($\\mathrm{\AA}$)’, fontsize=15)
    plt.ylabel(’probability density ($\\mathrm{\AA}^{-1}$)’, fontsize=15)

    energies = [’E = {: >5.2f} eV’.format(eigenvalues[i].real / e) for i in
                                          range(2)]
    plt.plot(r * 1e+10, densities[0], color=’blue’,  linewidth=’3’, label =
                                          energies[0])
    plt.plot(r * 1e+10, densities[1], color=’green’, linewidth=’3’, label =
                                          energies[1])
    plt.legend()
    plt.savefig(’finitediff.png’)
    plt.tight_layout()
    plt.show()
    return
‘‘‘ plot results ’’’
plot(r, densities, eigenvalues)
```

2.3 Another method:

Eq. (17) can be expressed as

$$-\frac{d^2\rho}{dr^2}-\frac{2\mu e^2}{4\pi\epsilon_0\hbar^2 r}\rho+\frac{\ell(\ell+1)}{r^2}\rho=\frac{2\mu E}{\hbar^2}\rho.$$

To make r dimensionless, we can rescale it by by $r'=\frac{r}{a}$, where $a\equiv\frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$ is the Bohr radius, we have

$$-\frac{1}{a^2}\frac{d^2\rho}{dr'^2}-\frac{2\rho}{a^2r'}+\frac{\ell(\ell+1)}{a^2r'^2}\rho=\frac{2\mu E}{\hbar^2}\rho.$$

This gives

$$-\frac{d^2\rho}{dr'^2}-\frac{2\rho}{r'}+\frac{\ell(\ell+1)}{r'^2}\rho=\frac{2\hbar^2(4\pi\epsilon_0)^2E}{\mu e^4}\rho.$$

Now defining a dimensionless energy,

$$E'\equiv\frac{E}{\frac{\mu e^4}{2\hbar^2(4\pi\epsilon_0)^2}}=\frac{E}{13.6\text{ eV}},$$

we can write the radial equation as

$$-\frac{d^2\rho}{dr'^2}-\frac{2\rho}{r'}+\frac{\ell(\ell+1)}{r'^2}\rho=E'\rho.$$

Now using finite difference method, we can solve the above Eigen-value problem by discretising r as $r'_j=j\Delta$. Thus the above equation can be written as

$$\frac{-\rho_{j+1}+2\rho_j-\rho_{j-1}}{\Delta^2}+\left[\frac{\ell(\ell+1)}{r'^2_j}-\frac{2}{r'_j}\right]\rho_j=E'\rho_j.$$

The term in parentheses is nothing but an effective potential V_{eff}. This is an eigenvalue problem where

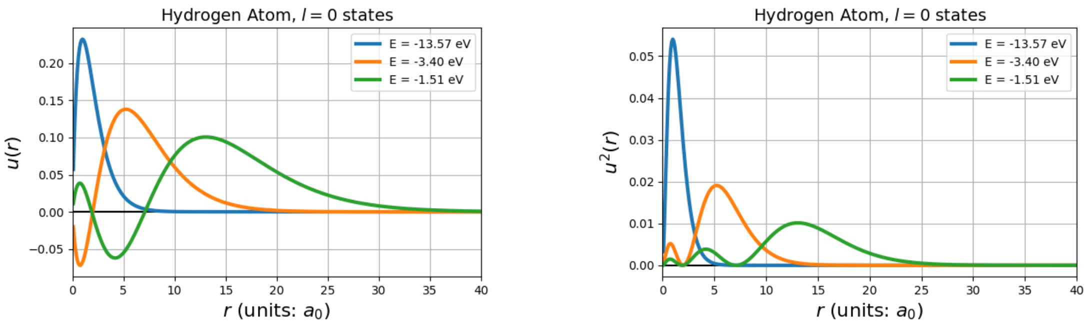
$$H_{ji}\psi_i=E'\psi_j,$$

with

$$H_{ji}=\begin{cases}\frac{2}{\Delta^2}+V_{\text{eff}}(r'_i) & \text{for} \quad i=j\\ -\frac{1}{\Delta^2} & \text{for} \quad i=j\pm1\\ 0 & \text{otherwise}\end{cases}$$

The eigenvalues give the energy of the states, and the eigenvectors are numerical approximations of the wave-functions.

```
import numpy as np
from scipy import linalg
from scipy import constants as const
import matplotlib.pyplot as plt
```



(a) (b)

Figure 3: Plot of eigenvalues, eigenfunctions, and probability density using dimensionless form of eigenvalue equation

```
’’’command for figures’’’
plt.rc(’figure’, figsize = (6, 4))
plt.rc(’axes’, labelsize=16, titlesize=14)
plt.rc(’figure’, autolayout = True)

’’’ Effective potential energy function’’’
def u(x):
    return l*(l+1)/x**2 - (2/x)

N = 2000    # Number of intervals
dim = N - 1 # Number of internal points
xl = 0      # xl corresponds to origin
xr = 200.
delta = (xr-xl)/N

x = np.linspace(xl+delta,xr-delta,dim)
l = 0       # orbital quantum number

#Fill Hamiltonian
h = np.zeros((dim,dim),float)
for i in range(len(h)-1):
        h[i,i+1] = h[i+1,i] = -1/delta**2
for i in range(len(h)):
        h[i,i] = 2./delta**2 + u(x[i])
vals, vecs = linalg.eigh(h)      #Note: eigenvectors in columns of vecs

’’’Wave function  ’’’
plt.figure()
```

```
plt.title("Hydrogen Atom, $\ell = 0$ states")
plt.xlabel("$r$ (units: $a_0$)")
plt.ylabel("$u(r)$")
plt.axhline(0, color=’black’)      #draw x axis
plt.grid(True)
plt.xlim(0,40)

energies = [’E = {: >5.2f} eV’.format(13.6*vals[i].real) for i in range(3)]
for n in range(3):
    y = np.transpose(vecs)[n]
    plt.plot(x,y, lw=’3’, label=energies[n])
    plt.legend()
    #print(’n = ’,n, ’, energy =’, energies[n])
plt.savefig(’2-dimless.png’)
plt.show()

’’’Probability Density ’’’
plt.figure()
plt.title("Hydrogen Atom, $\ell = 0$ states")
plt.xlabel("$r$ (units: $a_0$)")
plt.ylabel("$u^2(r)$")
plt.axhline(0, color=’black’)      #draw x axis
plt.grid(True)
plt.xlim(0,40)

for n in range(3):
    y = np.transpose(vecs)[n]
    plt.plot(x, y**2, lw=’3’, label=energies[n])
    plt.legend()
plt.show()
```