Solving Radial Schrödinger equation numerically

1 Radial Schrödinger equation

$$\frac{d^2\Psi(r)}{dr^2} + \left[\frac{2\mu E}{\hbar^2} - \frac{l(l+1)}{r^2} - U(r)\right]\Psi(r) = 0 \tag{1}$$

where,

$$U(r) = \frac{2\mu}{\hbar^2}V(r)$$

2 Dimensionless form

put, $r = xa_0$ where, $a_0 = \frac{4\pi\epsilon_0\hbar^2}{2\mu e^2} \approx 0.592$ Å and x is dimensionless.

$$\frac{d^2\Psi(x)}{a_0^2 dx^2} + \left[\frac{2\mu E}{\hbar^2} - \frac{l(l+1)}{a_0^2 x^2} - U(x)\right]\Psi(x) = 0$$

multiplying, a_0 on both sides gives:

$$\implies \frac{d^2\Psi(x)}{dx^2} + \left[\frac{2\mu a_0^2 E}{\hbar^2} - \frac{l(l+1)}{x^2} - a_0^2 U(x)\right]\Psi(x) = 0$$

$$\implies \frac{d^2\Psi(x)}{dx^2} + \left[\frac{E}{\frac{\hbar^2}{2\mu a_0^2}} - \frac{l(l+1)}{x^2} - W(x)\right]\Psi(x) = 0$$

$$\implies \frac{d^2\Psi(x)}{dx^2} + \left[\epsilon - \frac{l(l+1)}{x^2} - W(x)\right]\Psi(x) = 0 \quad \left(\epsilon = \frac{E}{E_1}\right) \text{ where, } E_1 = -\frac{\hbar^2}{2\mu a_0^2} \approx -13.6 \text{ eV}$$

where the negative energy represents bound states. For Hydrogen atom,

$$W(x) = a_0^2 U(r) = \frac{2\mu a_0^2}{\hbar^2}V(r) = \frac{2\mu a_0^2}{\hbar^2}\left(\frac{-e^2}{4\pi\epsilon_0 r}\right) = -\frac{2\mu a_0^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 a_0 x}\right) = -a_0\frac{1}{\frac{4\pi\epsilon_0\hbar^2}{2\mu e^2}}\frac{1}{x} = -\frac{2}{x} \quad \left(a_0 = \frac{4\pi\epsilon_0\hbar^2}{2\mu e^2}\right)$$

Therefore, the final dimensionless radial Schrödinger equation for Hydrogen atom is:

$$\frac{d^2\Psi(x)}{dx^2} + \left[\epsilon - \frac{l(l+1)}{x^2} + \frac{2}{x}\right]\Psi(x) = 0 \tag{2}$$

3 Numerov's algorithm

Discrete Taylor series expansion of Ψ_{i+1} about x_i

$$\begin{aligned}\Psi_{i+1} &= \Psi_i + (x_{i+1} - x_i)\Psi'\Big|_{x_i} + \frac{(x_{i+1} - x_i)^2}{2!}\Psi''\Big|_{x_i} + \frac{(x_{i+1} - x_i)^3}{3!}\Psi'''\Big|_{x_i} + \cdots \\ &= \Psi_i + h\Psi'_i + \frac{h^2}{2!}\Psi''_i + \frac{h^3}{3!}\Psi'''_i + \frac{h^4}{4!}\Psi''''_i + \cdots \end{aligned} \tag{3}$$

where,

$$\Psi'\Big|_{x_i} = \frac{d\Psi(r)}{dr}\Big|_{x_i} = \Psi'_i \quad \text{and } h = (x_{i+1} - x_i) \tag{4}$$

Discrete Taylor series expansion of Ψ_{i-1} about x_i

$$\begin{aligned}\Psi_{i-1} &= \Psi_i + (x_{i-1} - x_i)\Psi'\Big|_{x_i} + \frac{(x_{i-1} - x_i)^2}{2!}\Psi''\Big|_{x_i} + \frac{(x_{i-1} - x_i)^3}{3!}\Psi'''\Big|_{x_i} + \cdots \\ &= \Psi_i - h\Psi'_i + \frac{h^2}{2!}\Psi''_i - \frac{h^3}{3!}\Psi'''_i + \frac{h^4}{4!}\Psi''''_i + \cdots \end{aligned} \tag{5}$$

Adding Eq. (3) and Eq. (5) we get:

$$\begin{aligned}
\Psi_{i+1}+\Psi_{i-1} &= 2\Psi_i + h^2\Psi_i'' + \frac{h^4}{12}\Psi_i'''' + \cdots \\
\implies \Psi_{i+1}-2\Psi_i+\Psi_{i-1} &= h^2\Psi_i'' + \frac{h^4}{12}\Psi_i'''' + \cdots \qquad (6)\\
\implies \Psi_i'' &= \frac{\Psi_{i+1}-2\Psi_i+\Psi_{i-1}}{h^2} - \frac{h^2}{12}\Psi_i'''' \qquad (7)
\end{aligned}$$

ignoring the 4^{th} order term we get:

$$\Psi_i'' = \frac{\Psi_{i+1}-2\Psi_i+\Psi_{i-1}}{h^2} \tag{8}$$

How to find the 4^{th} order partial derivative term, Ψ'''' ? Write the LHS of Eq. (2) as:

$$\begin{aligned}
&\frac{d^2\Psi(x)}{dx^2} + \left[\epsilon - \frac{l(l+1)}{x^2} + \frac{2}{x}\right]\Psi(x) = s(x)\\
\implies &\frac{d^2\Psi(x)}{dx^2} + k^2(x)\Psi(x) = s(x) \quad \left(k^2(x) = \epsilon - \frac{l(l+1)}{x^2} + \frac{2}{x}\right)\\
\implies &\frac{d^2\Psi(x)}{dx^2} = s(x) - k^2(x)\Psi(x) \qquad (9)
\end{aligned}$$

$$\implies \frac{d^4\Psi(x)}{dx^4} = \frac{d^2}{dx^2}\left[s(x) - k^2(x)\Psi(x)\right]$$

Simplify it as

$$\begin{aligned}
\frac{d^4\Psi(x)}{dr^4} &= \frac{d^2}{dx^2}t(x) \quad \left[t(x) = s(x) - k^2(x)\Psi(x)\right]\\
\frac{d^4\Psi(x)}{dr^4} &= \frac{t_{i+1}-2t_i+t_{i-1}}{h^2} \quad \text{(Using Eq. (8))} \qquad (10)
\end{aligned}$$

Deriving the update equation: Putting, Eq. (10) in Eq. (7) we get:

$$\Psi_i'' = \frac{\Psi_{i+1}-2\Psi_i+\Psi_{i-1}}{h^2} - \frac{1}{12}\left(t_{i+1}-2t_i+t_{i-1}\right) \tag{11}$$

Putting the above equation in the Eq. (9) we get:

$$\frac{\Psi_{i+1}-2\Psi_i+\Psi_{i-1}}{h^2} - \frac{1}{12}\left(t_{i+1}-2t_i+t_{i-1}\right) = s_i - k_i^2\Psi_i$$

Again,

$$t(x) = s(x) - k^2(x)\Psi(x) \implies s(x) = t(x) + k^2(x)\Psi(x)$$

therefore,

$$\begin{aligned}
&\frac{\Psi_{i+1}-2\Psi_i+\Psi_{i-1}}{h^2} - \frac{1}{12}\left(t_{i+1}-2t_i+t_{i-1}\right) = t_i + k_i^2\Psi_i - k_i^2\Psi_i\\
\implies &\frac{\Psi_{i+1}-2\Psi_i+\Psi_{i-1}}{h^2} - \frac{1}{12}\left(t_{i+1}-2t_i+t_{i-1}\right) = t_i\\
\implies &\frac{\Psi_{i+1}-2\Psi_i+\Psi_{i-1}}{h^2} - \frac{1}{12}\left(t_{i+1}+10t_i+t_{i-1}\right) = 0\\
\implies &\frac{\Psi_{i+1}-2\Psi_i+\Psi_{i-1}}{h^2} - \frac{1}{12}\left(s_{i+1}-k_{i+1}^2\Psi_{i+1}+10\left(s_i-k_i^2\Psi_i\right)+s_{i-1}-k_{i-1}^2\Psi_{i-1}\right) = 0\\
\implies &\Psi_{i+1}-2\Psi_i+\Psi_{i-1} - \frac{h^2}{12}\left(s_{i+1}-k_{i+1}^2\Psi_{i+1}+10\left(s_i-k_i^2\Psi_i\right)+s_{i-1}-k_{i-1}^2\Psi_{i-1}\right) = 0\\
\implies &\Psi_{i+1}\left(1+\frac{h^2}{12}k_{i+1}^2\right) - 2\Psi_i\left(1-\frac{5h^2}{12}k_i^2\right) + \Psi_{i-1}\left(1+\frac{h^2}{12}k_{i-1}^2\right) - \frac{h^2}{12}\left(s_{i+1}+10s_i+s_{i-1}\right) = 0
\end{aligned}$$

For homogeneous case, $s(x) = 0$, therefore,

$$\frac{h^2}{12}\left(s_{i+1} + 10s_i + s_{i-1}\right) = 0$$

And we are left we the following **update equation**

$$\Psi_{i+1}\left(1 + \frac{h^2}{12}k_{i+1}^2\right) - 2\Psi_i\left(1 - \frac{5h^2}{12}k_i^2\right) + \Psi_{i-1}\left(1 + \frac{h^2}{12}k_{i-1}^2\right) = 0$$

where,

$$k_i^2 = \epsilon_n - \frac{l\left(l+1\right)}{x_i^2} + \frac{2}{x_i}, \quad \epsilon_n = \frac{E_n}{E_1} = -\frac{1}{n^2}\ \left(\text{where, } E_n = \frac{E_1}{n^2}\ \ n = 1, 2, 3, \cdots\right)$$

Put, $k_i^2 = g_i$, and $f_i = \left(1 + \frac{h^2}{12}k_i^2\right) = \left(1 + \frac{h^2}{12}g_i\right)$, such that the above equation can be written as:

$$\begin{aligned}
&\Psi_{i+1}f_{i+1} - 2\Psi_i\left(1 - \frac{5h^2}{12}g_i\right) + \Psi_{i-1}f_{i-1} = 0\\
\implies &\Psi_{i+1}f_{i+1} = -10\Psi_i\left(-\frac{1}{5} + \frac{h^2}{12}g_i\right) - \Psi_{i-1}f_{i-1}\\
\implies &\Psi_{i+1}f_{i+1} = -10\Psi_i\left(-1 - \frac{1}{5} + 1 + \frac{h^2}{12}g_i\right) - \Psi_{i-1}f_{i-1}\\
\implies &\Psi_{i+1}f_{i+1} = -10\Psi_i\left(-\frac{6}{5} + 1 + \frac{h^2}{12}g_i\right) - \Psi_{i-1}f_{i-1}\\
\implies &\Psi_{i+1}f_{i+1} = -10\Psi_i\left(-\frac{6}{5} + f_i\right) - \Psi_{i-1}f_{i-1}\\
\implies &\Psi_{i+1}f_{i+1} = \Psi_i\left(12 - 10f_i\right) - \Psi_{i-1}f_{i-1}\\
\implies &\Psi_{i+1} = \frac{\Psi_i\left(12 - 10f_i\right) - \Psi_{i-1}f_{i-1}}{f_{i+1}}
\end{aligned}$$

The final **update equation** is thus:

$$\boxed{\Psi_{i+1} = \frac{\Psi_i\left(12 - 10f_i\right) - \Psi_{i-1}f_{i-1}}{f_{i+1}}}$$

where,

$$f_i = \left(1 + \frac{h^2}{12}g_i\right) \quad \text{and } g_i = \epsilon_n - \frac{l\left(l+1\right)}{x_i^2} + \frac{2}{x_i}, \quad \text{with } \epsilon_n = -\frac{1}{n^2}\ \left(n = 1, 2, 3, \cdots\right)$$

n being the **Principal quantum number**.

4 References

Codes and explanation of the *Numerov's* method can be found in this github link

How to find the Eigen values numerically?

- **Method 1: (Matrix Numerov method)** Consider the one dimensional Schrödinger equation written in terms of dimensionless variables:

$$\left[\frac{d^2}{dx^2} - W\left(x\right)\right]\Psi\left(x\right) = -\epsilon\Psi\left(x\right) \tag{12}$$

where,

$$\epsilon = \frac{E}{E_1} \text{ with, } E_1 = \frac{\hbar^2}{2\mu a_0^2} \quad \text{and} \quad W(x) = a_0^2 U\left(r\right) = \frac{2\mu a_0^2}{\hbar^2}V\left(r\right), \quad \left(r = xa_0\right)$$

Here, a_0 is some arbitary constant, and not the Bohr's radius.

Eq. (12) is an Eigen value equation. Therefore we need to find the Eigen values of the operator,

$$\left[\frac{d^2}{dx^2} - W(x)\right]$$

Using the result,

$$\frac{d^2}{dx^2}\Psi(x) \equiv \Psi_i'' \approx \frac{\Psi_{i+1} - 2\Psi_i + \Psi_{i-1}}{h^2}$$

Putting the above equation in Eq. (12) we get,

$$\frac{\Psi_{i+1} - 2\Psi_i + \Psi_{i-1}}{h^2} + W_i\Psi_i = -\epsilon\Psi_i \tag{13}$$

We now construct a vector containing all the values of Ψ as:

$$\Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_{N-1} \\ \Psi_N \end{pmatrix}$$

Such that, Eq. (13) can be written in matrix form as:

$$\frac{1}{h^2}\begin{pmatrix} -2 & 1 & & & \\ 1 & -2 & 1 & & \\ & \ddots & \ddots & \ddots & \\ & & 1 & -2 & 1 \\ & & & 1 & -2 \end{pmatrix}\begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_{N-1} \\ \Psi_N \end{pmatrix} + \begin{pmatrix} W_1 & & & & \\ & W_2 & & & \\ & & \ddots & & \\ & & & W_{N-1} & \\ & & & & W_N \end{pmatrix}\begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_{N-1} \\ \Psi_N \end{pmatrix} = -\epsilon\begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_{N-1} \\ \Psi_N \end{pmatrix} \tag{14}$$

The above equation can be written as:

$$\left(\frac{1}{h^2}A + W\right)\Psi = -\epsilon\Psi \tag{15}$$

So all that is left is to find the Eigen values of the matrix, $\left(\frac{1}{h^2}A + W\right)$.

OR

$$\begin{aligned}
&\Psi_{i+1}\left(1 + \frac{h^2}{12}k_{i+1}^2\right) - 2\Psi_i\left(1 - \frac{5h^2}{12}k_i^2\right) + \Psi_{i-1}\left(1 + \frac{h^2}{12}k_{i-1}^2\right) = 0 \\
\implies &\Psi_{i+1}\left(1 + \frac{h^2}{12}(\epsilon_n - W_{i+1})\right) - 2\Psi_i\left(1 - \frac{5h^2}{12}(\epsilon_n - W_i)\right) + \Psi_{i-1}\left(1 + \frac{h^2}{12}(\epsilon_n - W_{i-1})\right) = 0 \;\left(k_i^2 = \epsilon_n - W_i(x_i)\right) \\
\implies &\frac{\Psi_{i+1} - 2\Psi_i + \Psi_{i-1}}{h^2} - \frac{\Psi_{i+1}W_{i+1} + 10\Psi_iW_i + \Psi_{i-1}W_{i-1}}{12} + \epsilon_n\frac{\Psi_{i+1} + 10\Psi_i + \Psi_{i-1}}{12} = 0 \\
\implies &-\frac{\Psi_{i+1} - 2\Psi_i + \Psi_{i-1}}{h^2} + \frac{\Psi_{i+1}W_{i+1} + 10\Psi_iW_i + \Psi_{i-1}W_{i-1}}{12} = \epsilon_n\frac{\Psi_{i+1} + 10\Psi_i + \Psi_{i-1}}{12}
\end{aligned}$$

where, for $i = 1$ the above equation is:

$$-\frac{\Psi_2 - 2\Psi_1 + \Psi_0}{h^2} + \frac{\Psi_2W_2 + 10\Psi_1W_1 + \Psi_0W_0}{12} = \epsilon_n\frac{\Psi_2 + 10\Psi_1 + \Psi_0}{12}$$

Assume, $\Psi_0 = 0$, this gives:

$$-\frac{\Psi_2 - 2\Psi_1}{h^2} + \frac{\Psi_2 W_2 + 10\Psi_1 W_1}{12} = \epsilon_n \frac{\Psi_2 + 10\Psi_1}{12}$$

for $i = 2$,

$$-\frac{\Psi_3 - 2\Psi_2 + \Psi_1}{h^2} + \frac{\Psi_3 W_3 + 10\Psi_2 W_2 + \Psi_1 W_1}{12} = \epsilon_n \frac{\Psi_3 + 10\Psi_2 + \Psi_1}{12}$$

for $i = 3$,

$$-\frac{\Psi_4 - 2\Psi_3 + \Psi_2}{h^2} + \frac{\Psi_4 W_4 + 10\Psi_3 W_3 + \Psi_2 W_2}{12} = \epsilon_n \frac{\Psi_4 + 10\Psi_3 + \Psi_2}{12}$$

Again, for $i = 4$,

$$-\frac{\Psi_5 - 2\Psi_4 + \Psi_3}{h^2} + \frac{\Psi_5 W_5 + 10\Psi_4 W_4 + \Psi_3 W_3}{12} = \epsilon_n \frac{\Psi_5 + 10\Psi_4 + \Psi_3}{12}$$

If the maximum number of points is 4, then $\Psi_5 = 0$

$$\implies -\frac{-2\Psi_4 + \Psi_3}{h^2} + \frac{10\Psi_4 W_4 + \Psi_3 W_3}{12} = \epsilon_n \frac{10\Psi_4 + \Psi_3}{12}$$

The above equations can be combined together in matrix form as:

$$\implies \left[-\frac{1}{h^2} \begin{pmatrix} -2 & 1 & 0 & 0 \\ 1 & -2 & 1 & 0 \\ 0 & 1 & -2 & 1 \\ 0 & 0 & 1 & -2 \end{pmatrix} + \frac{1}{12} \begin{pmatrix} 10W_1 & W_2 & 0 & 0 \\ W_1 & 10W_2 & W_3 & 0 \\ 0 & W_2 & 10W_3 & W_4 \\ 0 & 0 & W_3 & 10W_4 \end{pmatrix} \right] \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} = \frac{\epsilon_n}{12} \begin{pmatrix} 10 & 1 & 0 & 0 \\ 1 & 10 & 1 & 0 \\ 0 & 1 & 10 & 1 \\ 0 & 0 & 1 & 10 \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix}$$

$$\implies \left[-\frac{1}{h^2} \left(\mathbb{I}_{-1} - 2\mathbb{I}_0 + \mathbb{I}_1 \right) + \frac{1}{12} \left(\mathbb{I}_{-1} + 10\mathbb{I}_0 + \mathbb{I}_1 \right) W \right] \Psi = \frac{\epsilon_n}{12} \left(\mathbb{I}_{-1} + 10\mathbb{I}_0 + \mathbb{I}_1 \right) \Psi$$

$$\implies \left[-A + BW \right] \Psi = \epsilon_n B \Psi \quad \left(A = \frac{1}{h^2} \left(\mathbb{I}_{-1} - 2\mathbb{I}_0 + \mathbb{I}_1 \right),\ B = \frac{1}{12} \left(\mathbb{I}_{-1} + 10\mathbb{I}_0 + \mathbb{I}_1 \right) \right)$$

$$\implies \left[-B^{-1}A + W \right] \Psi = \epsilon_n \Psi \quad \left(W(x) = \frac{2ma_0^2}{\hbar^2} V(x),\ \epsilon_n = \frac{E_n}{E_0},\ E_0 = \frac{\hbar^2}{2ma_0^2} \right)$$

The energy eigen values evaluated using the above equation are going to be dimensionless. The equation below however will give the exact value of the energy eigen value.

$$\left[-\frac{\hbar^2}{2m} B^{-1} A + V \right] \Psi = E \Psi \quad \left(A \equiv \frac{A}{a_0^2} \right)$$

Here, $\mathbb{I}_p$ denotes a matrix who's p^{th} diagonal is unity

$$I_{-1} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, I_0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, I_1 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \text{ and } W = \begin{pmatrix} W_1 & 0 & 0 & 0 \\ 0 & W_2 & 0 & 0 \\ 0 & 0 & W_3 & 0 \\ 0 & 0 & 0 & W_4 \end{pmatrix}$$

So, we need to find the Eigen values and Eigen vectors of the matrix, $\left[-\frac{\hbar^2}{2m} B^{-1} A + V \right]$.

- **Method 2 (shooting method):** To find the Energy Eigen values we can also utilize the boundary conditions, such as

$$\Psi(r=0)=0; \qquad \Psi(r=\infty)=0 \quad \text{(for Hydrogen atom)}$$

Or

$$\Psi(x=\pm\infty)=0 \quad \text{(for one dimensional linear Harmonic oscillator)}$$

The boundary condition at ∞ can be implemented by choosing, some large, $r=r_c$ (say) such that, $\Psi(r_c)=0$.

For Hydrogen atom, if say, E_1 corresponds to a correct energy level, then when we backward integrate the radial wavefunction Numerov's method, we should get $\Psi(0)=0$. A deviation of the energy from E_1 will result in $\Psi(0)\neq 0$. The basic procedure to search for correct Energy Eigen value is thus as follows:

Start with a guess energy, E_1

  - 1) The guess energy, E_1 should be smaller than the smallest potential energy. In case of Hydrogen atom, it should be smaller than $-Z^2$.
  - 2) With the guess energy integrate the equation and get the value of the wavefunction at $r=0$, which we will denote as Ψ_1. Meanwhile, Set another energy, $E_2=E_1$.
  - 3) Increase the energy E_2 by an amount δE and get a new energy, $E_2=E_2+\delta E$.
  - 4) Integrate the Scrodinger equation to get the corresponding wavefunction, Ψ_2 and evaluate $\Psi_2(0)$.
  - 5) Go back to step 2 if $\Psi_1(0)\times\Psi_2(0)>0$.
  - 6) At this step, we should have the correct energy enclosed in the interval, $[E_1,E_2]$. Use root finding method, e.g. "*Newton Raphson method*", "*Secant method*", "*Brent's method*" etc. to get the correct energy.