

Solving Radial Schrödinger equation numerically

0.1 Radial Schrödinger equation

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

where,

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

0.2 Dimensionless form

put, $r = xa_0$ where, $a_0 = \frac{4\pi\epsilon_0\hbar^2}{2\mu e^2} \approx 0.592 \text{ \AA}$ 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:

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

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

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

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 is:

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

0.3 Numerov's method

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

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

where,

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

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

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

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

$$\Psi_{i+1} + \Psi_{i-1} = 2\Psi_i + h^2 \Psi''_i + \frac{h^4}{12} \Psi''''_i + \dots$$

$$\implies \Psi_{i+1} - 2\Psi_i + \Psi_{i-1} = h^2 \Psi_i'' + \frac{h^4}{12} \Psi_i'''' + \dots \quad (6)$$

$$\implies \Psi_i'' = \frac{\Psi_{i+1} - 2\Psi_i + \Psi_{i-1}}{h^2} - \frac{h^2}{12} \Psi_i'''' \quad (7)$$

ignoring the 4th order term we get:

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

How to find the 4th order term ? Write the LHS of Eq. (2) as:

$$\begin{aligned} & \frac{d^2 \Psi(x)}{dx^2} + \left[\epsilon - \frac{l(l+1)}{x^2} + \frac{2}{x} \right] \Psi(x) = s(x) \\ \implies & \frac{d^2 \Psi(x)}{dx^2} + k^2(x) \Psi(x) = s(x) \quad \left(k^2(x) = \epsilon - \frac{l(l+1)}{x^2} + \frac{2}{x} \right) \\ \implies & \frac{d^2 \Psi(x)}{dx^2} = s(x) - k^2(x) \Psi(x) \\ \implies & \frac{d^4 \Psi(x)}{dx^4} = \frac{d^2}{dx^2} [s(x) - k^2(x) \Psi(x)] \end{aligned} \quad (9)$$

Simplify it as

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

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

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

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

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

Again,

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

therefore,

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

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

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

And we are left with 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,

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

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:

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

The final **update equation** is thus:

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

where,

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

n being the **Principal quantum number**.

0.4 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:** Consider the dimensionless Radial Schrödinger equation with azimuthal quantum number, $l = 0$:

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

where,

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

Here, a_0 is some arbitrary 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,

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

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:

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

The above equation can be written as:

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

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

OR

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

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 $\Psi_5 = 0$

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

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

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

- **Method 2 (shooting method):** To find the Energy Eigen values we will utilize the boundary conditions:

$$\Psi(0) = 0; \quad \Psi(\infty) = 0 \quad (16)$$

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

Start with a guess energy,

- 1) The guess energy, E_1 should be smaller than the smallest potential energy. In our case, 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, $E_2 = E_1 + \delta E$.
- 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. *"Brent's method"* to get the correct energy.