

1 Numerov method

The Numerov method is a general numerical method to solve second order differential equation of the form

$$\frac{d^2y}{dx^2} + g(x)y(x) - s(x) = 0 \quad (1)$$

where $g(x)$ and $s(x)$ are continuous function on the domain $[a,b]$. To solve this equation we will need to solve this problem as a boundary value problem : $y(a)$ and $y(b)$ are known. At this point, the first thing we need to do is to discretize the interval $[a,b]$ using equally spaced points. Let's say that we fix the distance between each point as h , then we obtain a discrete domain as illustrated in figure (1) below.

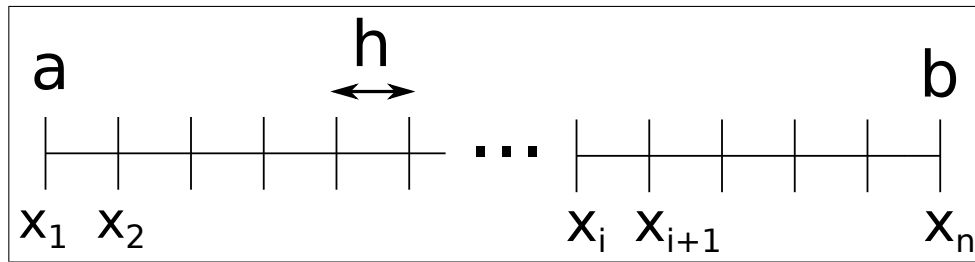


FIGURE 1 – The new one dimensional interval after discretization

Then the solution $y(x)$ is also obtain as a discrete set of point for each x_i . This means that we now have $y(x) = y(x_i) = y_i$, and the equation becomes

$$\frac{d^2y_i}{dx^2} + g_i(x)y_i(x) + s_i(x) = 0 \quad (2)$$

To obtain the wanted relation we start by writing the Taylor expansion of the function $y(x)$ around x_0 :

$$y(x) = y(x_0) + y'(x_0)(x - x_0) + \frac{y''(x)}{2!}(x - x_0)^2 + \frac{y^{(3)}(x)}{3!}(x - x_0)^3 + \dots \quad (3)$$

If we denote the space between x and x_0 by $h = x - x_0$, we can write the above equation as

$$y(x + h) = y(x) + hy'(x) + \frac{h^2}{2}y''(x) + \frac{h^3}{6}y^{(3)}(x) + \frac{h^4}{24}y^{(4)}(x) + \frac{h^5}{5!}y^{(5)}(x) + \dots \quad (4)$$

Similarly for the expansion around $x - h$:

$$y(x + h) = y(x) - hy'(x) + \frac{h^2}{2}y''(x) - \frac{h^3}{6}y^{(3)}(x) + \frac{h^4}{24}y^{(4)}(x) - \frac{h^5}{5!}y^{(5)}(x) + \dots \quad (5)$$

Then by adding equation 4 and 5, we obtain

$$y(x+h) + y(x-h) = 2y(x) + h^2 y''(x) + \frac{h^4}{12} y^{(4)}(x) + O(h^6) \quad (6)$$

Wich is equivalent, by using the discrete notation, to :

$$y_{i+1} = -y_{i-1} + 2y_n + y''_n h^2 + \frac{1}{12} y^{(4)}_n h^4 + O(h^6) \quad (7)$$

Now, to solve this equation for $y_n + 1$ we have to obtain expressions for $y''(x)$ and $y^{(4)}(x)$. First, for $y''(x)$, we use its expression given in equation 1 : $y''(x) = -g(x)y(x) + s(x)$. To get an expression for $y^{(4)}(x)$, we use another time expression 1 : we difference $y''(x) = -g(x)y(x) + s(x)$ twice and approximate it the same way we did above.

$$y^{(4)}_i = \frac{d^2}{dx^2}(-g_i y_i + s_i) \quad (8)$$

$$h^2 y^{(4)}_i = -g_{i+1} y_{i+1} + s_{i+1} + 2g_n y_n - 2s_n - g_{i-1} y_{i-1} + s_{i-1} + O(h^4) \quad (9)$$

If we now substitute y''_i and $y^{(4)}_i$ in 7, we obtain the expression we are looking for :

$$y_{i+1} + y_{i-1} = 2y_i + h^2(-g_i y_i + s_i) + \frac{h^2}{12}(-g_{i+1} y_{i+1} + s_{i+1} + 2g_i y_i - 2s_i - g_{i-1} y_{i-1} + s_{i-1}) + O(h^6) \quad (10)$$

If we neglect the term of order h^6 this yields the Numerov method :

$$y_{i+1} = \frac{2y_i \left(1 - \frac{5h^2}{12} g_i\right) - y_{i-1} \left(1 + \frac{h^2}{12} g_{i-1}\right) + \frac{h^2}{12}(s_{i+1} + 10s_i + s_{i-1})}{1 + \frac{h^2}{12} g_{i+1}} \quad (11)$$

So with this relation, we can now find the value of the solution to the differential equation at different discrete points y_{i+1} if we have its value at two points (y_{i-1}, y_i) . So, because we have a discrete interval (see figure (1)), all we have to do to find an approximate solution is to find the value of the two first points (x_1 and x_2) then we use the Numerov method 11 to find all the following points in the interval $[a, b]$.

2 Schrödinger equation

In this script the Numerov method is used to solve the one-dimensionnal time-independant Schrödinger equation. The one-dimensional time-independant Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi(x) = E \psi(x) \quad (12)$$

where $\psi(x)$ is the wavefunction, $V(x)$ the potential energy, m the mass and \hbar the reduced Planck constant. This formula would be hard to compute because of the

very small values of \hbar and m ($\hbar = 1.05457 \cdot 10^{-34}$ and $m_e = 9.11 \cdot 10^{-31}$), so to avoid dealing with these quantities we use the atomic unit system. In this system, the value of the four following fundamentals physical constants are unity : the reduced Planck constant \hbar , the elementary charge e , the electron mass m_e and Coulomb's constant $k_e = \frac{1}{4\pi\epsilon_0}$. So in this unit system, Schrödinger's equation is simply :

$$\frac{d^2\psi(x)}{dx^2} + 2(E - V(x))\psi(x) = 0 \quad (13)$$

This function respects the general form of equation 1 with $g(x) = 2(E - V(x))$ and $s(x) = 0$. So we can use the Numerov method with this differential equation and equation 11 becomes

$$\psi_{i+1} = \frac{2 \left(1 - \frac{5}{12}h^2g_i\right) \psi_i - \left(1 + \frac{1}{12}h^2g_{i-1}\right) \psi_{i-1}}{1 + \frac{1}{12}h^2g_{i+1}} \quad (14)$$

But how can we use this relation to solve Schrodinger equation ? Remember that we mentionned in the last section that to use this method we needed to know the first two points of a discrete interval where we knew the limits conditions. So the first thing to do is define an intervall where we will find the approximate wave function.

The problem is that the wave function has a domain that goes from ∞ to $-\infty$. So for most cases, the wave function isn't only defined in a small definite intervall. But to help us resolve this issue, we can use the fact that the wave function must also respect these conditions :

1. $\psi(x) \rightarrow 0$ as $x \rightarrow \pm\infty$
2. $\int_{-\infty}^{\infty} \psi(x)dx = 1$
3. $\psi(x)$ and $\psi'(x)$ are continuous

To define our interval we can use the first condition : we find two points where the wave function converges uniformly to zero and is very close to zero, let's call them x_a and x_b , at these points we set the wave function at zero ($\psi(x_a) = 0$ and $\psi(x_b) = 0$). We then have an intervall ($[x_a, x_b]$) where we know the limits conditions ($x_a = 0$ and $x_b = 0$).

Our next issue is to find these two points where we will set the wave function at zero. To help us, we will restrict our method to bound states (in quantum physics, a bound state is a special quantum state of a particle subject to a potential such that the particle has a tendency to remain localised in one or more regions of space). In such a state, the energy levels are always lower than the maximum value of the potential in the region where the particule is localised. In fact, for a certain energy level, we can define a classically allowed region corresponding to a potential energy lower than the energy level and a classically forbidden region corresponding to a potential energy greater than the energy of the particule. Such regions are illustrated in figure (2).

Furthermore, according to the Born interpretation, the square of the module of the wave function represents the probability density to find the particule at a certain point. Such a probability will fastly decrease in the classically forbidden region (because the particule doesn't have a great probability to be found in such a region). In fact, if we look at potential that have an analytic solution such as the

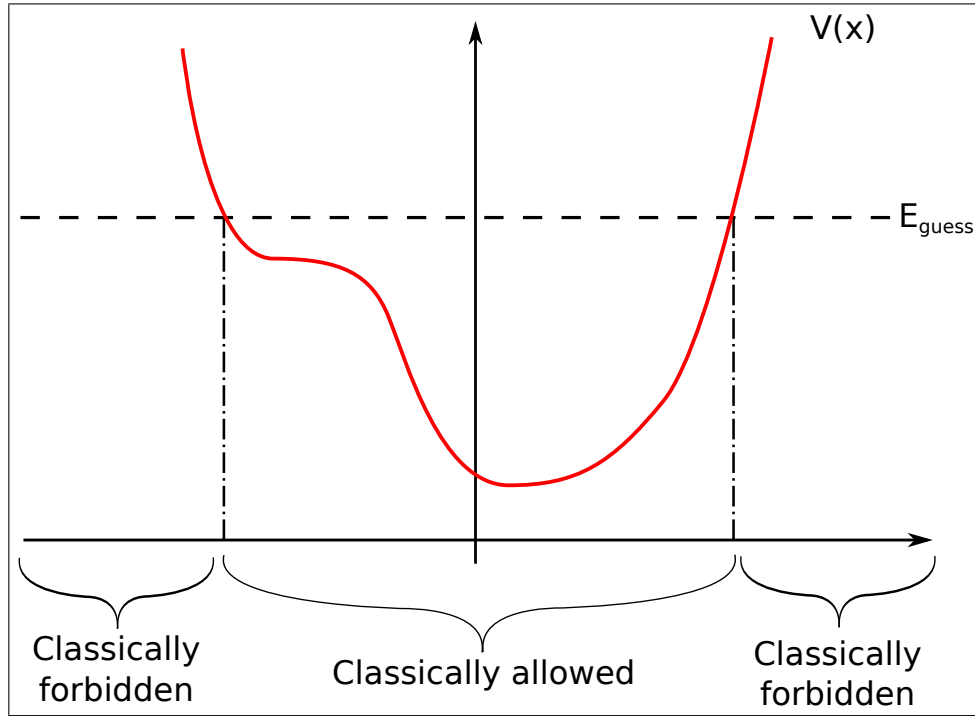


FIGURE 2 – The classically allowed and forbidden region for a given potential $V(x)$ and an energy guess E_{guess}

harmonic potential ($V(x) = x^2$), we can see that in the classically forbidden region the wave function is very small and uniformly converges to zero. We can see this in

Thus, all we have to do to define an interval with known borders value is to go deep into the classically forbidden region and fix the wave function at zero at this point. We then have an interval that goes from x_{min} to x_{max} and where the wave function is zero.

Now that we have our interval we can discretize it with points equally spaced (of distance h) and an approximate wave function. To do so, all we have to do is start from x_{min} , then we define an initial augmentation that corresponds to the value of the wave function at the point x_{min+1} (this value is arbitrary, it doesn't change the general look of the wave function, it only multiplies the wave function by an arbitrary numerical value). Then knowing these two points, we can use relation 14 to find the value of the wave function for all the other points in the interval. But to use equation 14 we need to make an energy guess. This is the crucial point : the wave function will only respect the second boundary condition ($\psi(x_{max}) = 0$) if the energy guess corresponds to an allowed energy level. Then, we need to recursively make energy guess and calculate the wave function until we find one that respects the conditions at x_{min} and x_{max} .

To synthesize, to find the energy levels, all we have to do is follow this procedure :

1. Make a guess for an energy level
2. Find the smallest and the greatest meeting points of the potential with this energy (x_a and x_b)
3. With these points, go deep into the classically forbidden area and fix the

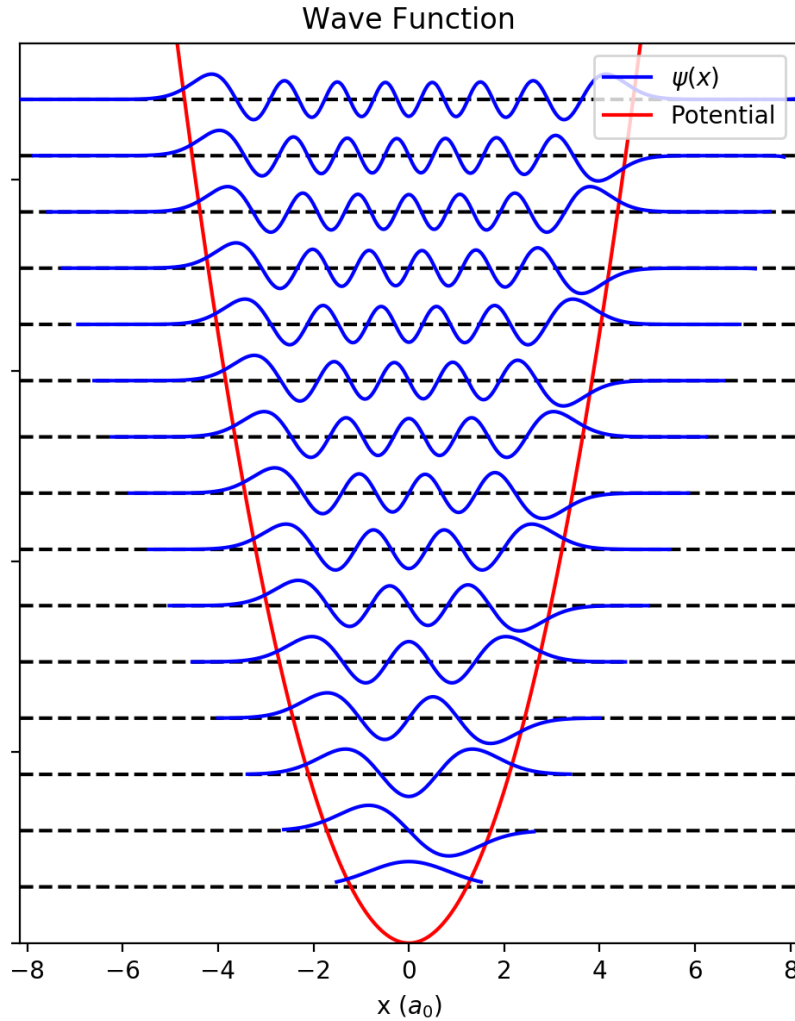


FIGURE 3 – Wave function for the harmonic potential (in a.u.)

wave function at zero for two points ($\psi(x_{min}) = \psi(x_{max}) = 0$) that define the intervall

4. Discretize the intervall $[x_{min}, x_{max}]$ with the desired number of point (Nbr_division)
5. Define an arbitrary initial augumentaion for the value of the wave function at x_{min+1}
6. With relation 14 find the value for the wave function at all the other points in the intervall
7. To verify that E_{guess} corresponds to an energy levels verify if the value of the wave function at the point x_{max} is approximately zero ($\psi(x_{max}) \approx 0$)
8. If it doesn't respect this condition make a new energy guess

There is still one question that we left unanswered : if I have an energy guess that repsects the conditions, how do I know if this energy levels correponds to the ground state of the third exited state? To fix this problem all we have to do is

use the following theorem : for the one-dimensional time-independant Schrödinger equation, the energy level for a given wave function corresponds to the number of nodes (the number of times $\psi(x) = 0$) rejecting those when $x \rightarrow \pm\infty$. To visualize this theorem, we can see on figure (2) that the lowest wave function corresponds to the ground state E_0 , that the second has one node so it corresponds to the first excited state E_1 , etc.

3 Algorithm

(To be continued)

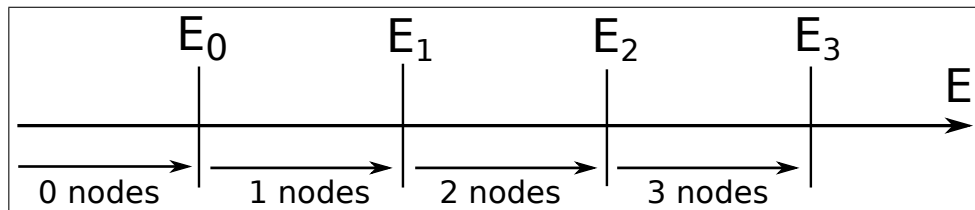


FIGURE 4 – The energy levels evolution with the number of nodes