TPMN 2019/2020 : Solving the Schrödinger equation

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- **Aim of this course :** Solving the Sch¨odinger equation by using a computer

$$H\Psi(r) = \varepsilon\Psi(r)$$

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- **Aim of this course :** Solving the Sch¨odinger equation by using a computer

$$H\Psi(r) = s\Psi(r)$$

- Three kind of terms
  - H, the Hamiltonian operator → it describes the quantum system ; in general it is known
  - $\Psi(r)$, the wavefunction of the system ; we want to compute it
  - s, the total energy of the system ; we want to compute it

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- Three kind of terms
  - H, the Hamiltonian operator → it describes the quantum system ; in general it is known
  - $\Psi(\mathbf{r})$, the wavefunction of the system ; we want to compute it
  - ε, the total energy of the system ; we want to compute it
- **Problem :** the Schr¨odinger equation is an eigenvalue problem → to get $\Psi(\mathbf{r})$ we need ε
  we to get ε we need $\Psi(\mathbf{r})$!

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  - *H*, the Hamiltonian operator → it describes the quantum system ; in general it is known
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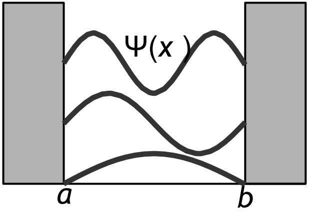
  - s, the total energy of the system ; we want to compute it
- **Problem :** the Schr¨odinger equation is an eigenvalue problem → to get $\Psi(r)$ we need s

  we to get s we need $\Psi(r)$!
- From a numerical point of view, there are different ways to solve this problem
  - Tomorrow, we will see a quite general method : the **Finite Difference Method**
  - Next week, R. Hertel will present another possible way to proceed : the **Finite Element Method**

The Numerov algorithm

- **The problem to solve : Free particule in a box (1D)**



The Numerov algorithm

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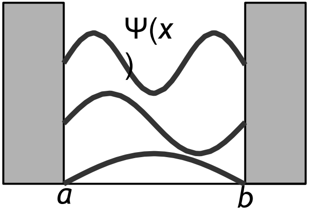
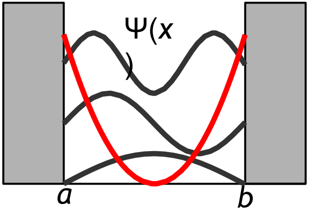


$$\boxed{-\frac{1}{2}\frac{d^2\Psi}{dx^2} = s\Psi}$$

The Numerov algorithme

The problem to solve : Free particule in a box (1D)



$$\boxed{-\frac{1}{2}\frac{d^2\Psi}{dx^2} = s\Psi}$$

$$\boxed{-\frac{1}{2}\frac{d^2\Psi}{dx^2} + V(x)\Psi(x) = s\Psi}$$

The Numerov algorithme

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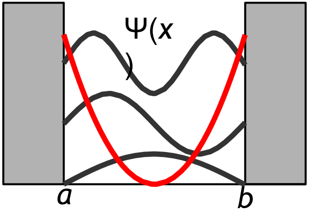


$$\boxed{-\frac{1}{2}\frac{d^2\Psi}{dx^2} = s\Psi}$$

$$\boxed{-\frac{1}{2}\frac{d^2\Psi}{dx^2} + V(x)\Psi(x) = s\Psi}$$

This differential equation belongs to the general kind of 2nd order linear differential equation

$$\boxed{\frac{d^2\Psi}{dx^2} + Q(x)\Psi(x) = S(x)}$$

where $Q(x)$ and $S(x)$ are continuous functions on a domain $[a, b]$. The equation is to be solved as a **boundary value problem**, *i.e.*, $\Psi(a)$ and $\Psi(b)$ are given.

The Numerov algorithm

$$\boxed{\frac{d^2\Psi}{dx^2} + Q(x)\Psi(x) = S(x)}$$

Depending of the functions $Q(x)$ and $S(x)$, the Numerov algorithm can be used to solve

- Eigenvalue problem: $Q(x) \neq 0$ and $S(x) = 0$
  - The Schrödinger equation
  - Ex. : Hydrogen atom

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}) \xrightarrow{\text{spherical symmetry}} \psi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r}Y_{lm}(\theta,\phi)$$

$Y_{lm}(\theta, \phi)$ are the spherical harmonics and the function $u(r)$ is given by 2nd order differential equation

$$\boxed{\frac{d^2u}{dr^2} = -Q(r)u(r)} \text{ with } Q(r) = 2\varepsilon + \frac{2Z}{r} - \frac{l(l+1)}{r^2}$$

The Numerov algorithm

$$\boxed{\frac{d^2\Psi}{dx^2} + Q(x)\Psi(x) = S(x)}$$

Depending of the functions $Q(x)$ and $S(x)$, the Numerov algorithm can be used to solve

- Linear system problem: $Q(x) = 0$
  - The 1D Poisson equation
  - Ex. : Hartree potentiel in spherical symmetry

$$V_{Hartree}(\mathbf{r}) = \frac{e^2}{4\pi\varepsilon_0}\int d^3\mathbf{r}'\,\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \xrightarrow{\text{Spherical symmetry}} \frac{d^2U_{Hartree}}{dr^2} = -4\pi r\,\rho(r)$$

$$U_{Hartree}(r) = rV_{Hartree}(r) \quad \Rightarrow \quad \boxed{\frac{d^2U_{Hartree}}{dr^2} = S(r)}$$

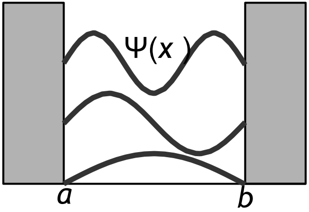
$$S(r) = 4\pi r\,\rho(r)$$

$$Q(x) = 0$$

The Numerov algorithm

$$\boxed{\frac{d^2\Psi}{dx^2} + Q(x)\Psi(x) = S(x)}$$

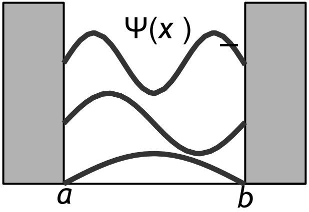
The problem to solve : Free particule in a box (1D)



The Numerov algorithme

$$\boxed{\frac{d^2\Psi}{dx^2} + Q(x)\Psi(x) = S(x)}$$

The problem to solve : Free particule in a box (1D)



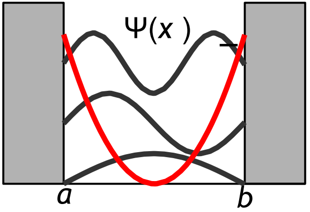
$$\frac{1}{2}\frac{d^2\Psi}{dx^2} = s\Psi$$

$$\boxed{\begin{aligned} &\frac{d^2\Psi}{dx^2} + 2s\Psi(x) = 0 \\ &Q(x) = 2s \\ &S(x) = 0 \end{aligned}}$$

The Numerov algorithme

$$\frac{d^2\Psi}{dx^2} + Q(x)\Psi(x) = S(x)$$

The problem to solve : Free particule in a box (1D)



$$\frac{1}{2}\frac{d^2\Psi}{dx^2} = s\Psi$$

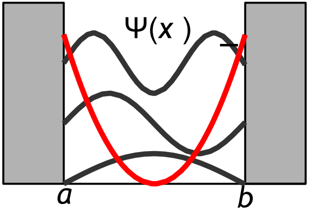
$$\boxed{\begin{array}{l} \frac{d^2\Psi}{dx^2} + 2s\Psi(x) = 0 \\ Q(x) = 2s \\ S(x) = 0 \end{array}}$$

$$-\frac{1}{2}\frac{d^2\Psi}{dx^2} + V(x)\Psi(x) = s\Psi$$

The Numerov algorithme

$$\frac{d^2\Psi}{dx^2} + Q(x)\Psi(x) = S(x)$$

The problem to solve : Free particule in a box (1D)



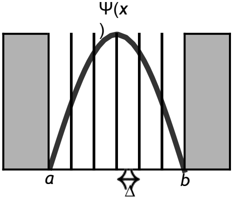
$$\frac{1}{2}\frac{d^2\Psi}{dx^2} = s\Psi$$

$$\frac{d^2\Psi}{dx^2} + 2s\Psi(x) = 0$$
$$Q(x) = 2s$$
$$S(x) = 0$$

$$-\frac{1}{2}\frac{d^2\Psi}{dx^2} + V(x)\Psi(x) = s\Psi$$

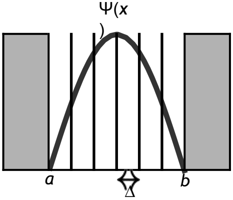
$$\frac{d^2\Psi}{dx^2} + 2(s - V(x))\Psi(x) = 0$$
$$Q(x) = 2(s - V(x))$$
$$S(x) = 0$$

The Numerov algorithm



- We consider a grid, step Δ,

The Numerov algorithm

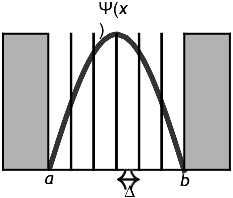


- We consider a grid, step Δ,
- We resort to Taylor series to express $\Psi(x+\Delta)$ and $\Psi(x-\Delta)$

$$\Psi(x+\Delta) = \Psi(x) + \Delta\frac{d\Psi(x)}{dx} + \frac{\Delta^2}{2}\frac{d^2\Psi(x)}{dx^2} + \frac{\Delta^3}{6}\frac{d^6\Psi(x)}{dx^6} + \frac{\Delta^4}{24}\frac{d^4\Psi(x)}{dx^4} + O(\Delta^5)$$

$$\Psi(x-\Delta) = \Psi(x) - \Delta\frac{d\Psi(x)}{dx} + \frac{\Delta^2}{2}\frac{d^2\Psi(x)}{dx^2} - \frac{\Delta^3}{6}\frac{d^6\Psi(x)}{dx^6} + \frac{\Delta^4}{24}\frac{d^4\Psi(x)}{dx^4} - O(\Delta^5)$$

The Numerov algorithm



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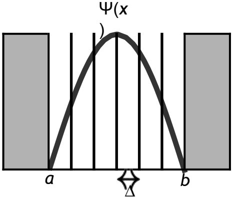
- By summing the above expressions

$$\Psi(x+\Delta) + \Psi(x-\Delta) - 2\Psi(x) = \Delta^2\frac{d^2\Psi(x)}{dx^2} + \frac{\Delta^4}{12}\frac{d^4\Psi(x)}{dx^4} + O(\Delta)^6$$

The Numerov algorithm



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- We resort to Taylor series to express $\frac{d^2\Psi(x+\Delta)}{dx^2}$ and $\frac{d^2\Psi(x-\Delta)}{dx^2}$

$$\frac{d^2\Psi(x+\Delta)}{dx^2} = \frac{d^2\Psi(x)}{dx^2} + \Delta\frac{d^3\Psi(x)}{dx^3} + \frac{\Delta^2}{2}\frac{d^4\Psi(x)}{dx^4} + O(\Delta^3)$$

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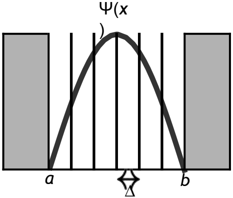

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$$\Psi(x+\Delta) + \Psi(x-\Delta) - 2\Psi(x) = \Delta^2\frac{d^2\Psi(x)}{dx^2} + \frac{\Delta^4}{12}\frac{d^4\Psi(x)}{dx^4} + O(\Delta)^6$$

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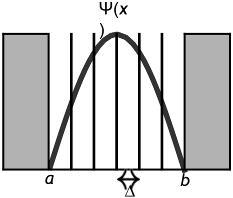
- By summing the above expressions

$$\frac{d^2\Psi(x+\Delta)}{dx^2} + \frac{d^2\Psi(x-\Delta)}{dx^2} - 2\frac{d^2\Psi(x)}{dx^2} = \Delta^2\frac{d^4\Psi(x)}{dx^4} + O(\Delta)^5$$

The Numerov algorithm



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$$\Psi(x+\Delta) + \Psi(x-\Delta) - 2\Psi(x) = \Delta^2\frac{d^2\Psi(x)}{dx^2} + \frac{\Delta^4}{12}\frac{d^4\Psi(x)}{dx^4} + O(\Delta)^6$$

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$$\frac{d^2\Psi(x-\Delta)}{dx^2} = \frac{d^2\Psi(x)}{dx^2} - \Delta\frac{d^3\Psi(x)}{dx^3} + \frac{\Delta^2}{2}\frac{d^4\Psi(x)}{dx^4} - O(\Delta)^3$$

- By summing the above expressions

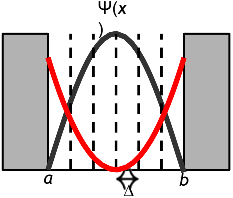
$$\frac{d^2\Psi(x+\Delta)}{dx^2} + \frac{d^2\Psi(x-\Delta)}{dx^2} - 2\frac{d^2\Psi(x)}{dx^2} = \Delta^2\frac{d^4\Psi(x)}{dx^4} + O(\Delta)^5$$

- we get

$$\Psi(x+\Delta) + \Psi(x-\Delta) - 2\Psi(x) = \frac{\Delta^2}{12}\left[\frac{d^2\Psi(x+\Delta)}{dx^2} + \frac{d^2\Psi(x-\Delta)}{dx^2} + 10\frac{d^2\Psi(x)}{dx^2}\right] + O(\Delta)^6$$

The Numerov algorithm

- Now from $\Psi(x+\Delta)+\Psi(x-\Delta)-2\Psi(x) = \frac{\Delta^2}{12}\left[\frac{d^2\Psi(x+\Delta)}{dx^2}+\frac{d^2\Psi(x-\Delta)}{dx^2}+10\frac{d^2\Psi(x)}{dx^2}\right]+O(\Delta)^6$
- Since $\frac{d^2\Psi}{dx^2} = -Q(x)\Psi(x)+S(x)$, we get
- we get



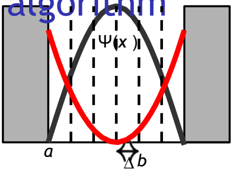
$$\left[1+\frac{\Delta^2}{12}Q(x+\Delta)\right]\Psi(x+\Delta) = -\left[1+\frac{\Delta^2}{12}Q(x-\Delta)\right]\Psi(x-\Delta) + 2\left[1-\frac{5\Delta^2}{12}Q(x)\right]\Psi(x) + \frac{\Delta^2}{12}\left(S(x+\Delta)+S(x-\Delta)+10S(x)\right)+O(\Delta^6)$$

$$\frac{d^2\Psi}{dx^2}+2\left(s-V(x)\right)\Psi(x)=0$$

$$Q(x)=2\left(s-V(x)\right)$$

$$S(x)=0$$

The Numerov algorithm



$$\frac{d^2\Psi}{dx^2} + 2(s - V(x))\Psi(x) = 0$$
$$Q(x) = 2(s - V(x))$$
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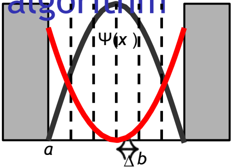
$$\left(1 + \frac{\Delta^2}{12} Q(x+\Delta)\right)\Psi(x+\Delta) = -\left(1 + \frac{\Delta^2}{12} Q(x-\Delta)\right)\Psi(x-\Delta) + 2\left(1 - \frac{5\Delta^2}{12} Q(x)\right)\Psi(x) + \frac{\Delta^2}{12}\left(S(x+\Delta) + S(x-\Delta) + 10S(x)\right) + O(\Delta^6)$$

- The potential, $V(x)$ is known ;
- If we set a value for the total energy of the particule in the box, $s \rightarrow Q(x) = 2(s - V(x))$ is known
- the value of the wavefunction at $x = a$ is known : $\Psi(a) = 0$; if we set a value for the wavefunction at $a + \Delta$, then we get the value of the wavefunction at $a + 2\Delta$
$$\left(1 + \frac{\Delta^2}{12} Q(a+2\Delta)\right)\Psi(a+2\Delta) = -\left(1 + \frac{\Delta^2}{12} Q(a)\right)\Psi(a) + 2\left(1 - \frac{5\Delta^2}{12} Q(a+\Delta)\right)\Psi(a+\Delta)$$
- Then from $\Psi(a+\Delta)$ and $\Psi(a+2\Delta)$, we can compute $\Psi(a+3\Delta)$, and so on ...

$\longrightarrow$ **Outward integration**

The Numerov algorithm



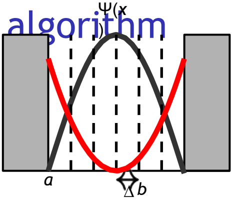
$$\frac{d^2\Psi}{dx^2} + 2\,(s - V(x))\,\Psi(x) = 0$$
$$Q(x) = 2\,(s - V(x))$$
$$S(x) = 0$$

$$\left(1 + \frac{\Delta^2}{12} Q(x+\Delta)\right) \Psi(x+\Delta) = -\left(1 + \frac{\Delta^2}{12} Q(x-\Delta)\right) \Psi(x-\Delta) + 2\left(1 - \frac{5\Delta^2}{12} Q(x)\right) \Psi(x) + \frac{\Delta^2}{12}\left(S(x+\Delta) + S(x-\Delta) + 10 S(x)\right) + O(\Delta^6)$$

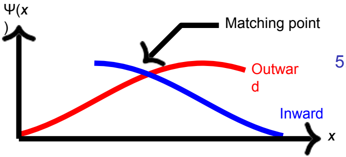
- The potential, $V(x)$ is known ;
- If we set a value for the total energy of the particule in the box, $s \rightarrow Q(x) = 2(s - V(x))$ is known
- the value of the wavefunction at $x = b$ is known : $\Psi(b) = 0$; if we set a value for the wavefunction at $b - \Delta$, then we get the value of the wavefunction at $b - 2\Delta$
$$\left(1 + \frac{\Delta^2}{12} Q(b - 2\Delta)\right) \Psi(b - 2\Delta) = -\left(1 + \frac{\Delta^2}{12} Q(b)\right) \Psi(b) + 2\left(1 - \frac{5\Delta^2}{12} Q(b - \Delta)\right) \Psi(b - \Delta)$$
- Then from $\Psi(b - \Delta)$ and $\Psi(b - 2\Delta)$, we can compute $\Psi(b - 3\Delta)$, and so on ...

$\longrightarrow$ **Inward integration**

The Numerov algorithm



$$\frac{d^2\Psi}{dx^2} + 2\,(s - V(x))\,\Psi(x) = 0$$
$$Q(x) = 2\,(s - V(x))$$



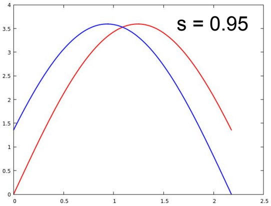
Write a code to compute the wavefunctions of the free particule in a box

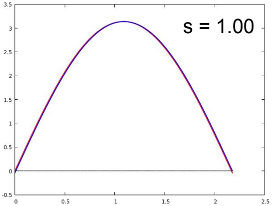
1. Set a guest value for s
2. Perform an inward integration from a to x_m, the matching point. The matching point is necessary to get the right value of the energy ; in the case of free particle in box problem, a good way to choose the matching point is to take a point where the value of the wavefunctions is different from zero and close to the middle of the box.
3. Perform an outward integration from b to x_m
4. Compute the ratios of the first derivative of the wavefunction over the amplitude for both in- and out-ward wavefunctions at the matching point. Change the value of s so that these ratios are identical for both in- and out-ward wavefunctions.
5. Compare the numerical results with the analytical ones.

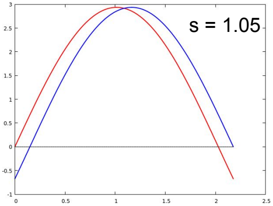
$$\left(1 + \frac{\Delta^2}{12} Q(a + 2\Delta)\right) \Psi(a + 2\Delta) = -\left(1 + \frac{\Delta^2}{12} Q(a)\right) \Psi(a) + 2\left(1 - \frac{5\Delta^2}{12} Q(a + \Delta)\right) \Psi(a + \Delta)$$

$$\left(1 + \frac{\Delta^2}{12} Q(b - 2\Delta)\right) \Psi(b - 2\Delta) = -\left(1 + \frac{\Delta^2}{12} Q(b)\right) \Psi(b) + 2\left(1 - \frac{5\Delta^2}{12} Q(b - \Delta)\right) \Psi(b - \Delta)$$

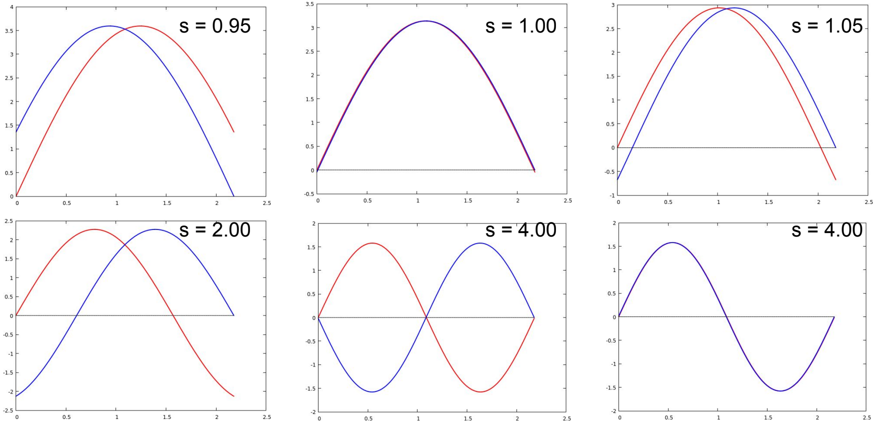
The Numerov algorithm



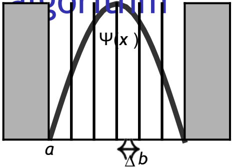




The Numerov algorithm



The Numerov algorithm



$$\boxed{-\frac{1}{2}\frac{d^2\Psi}{dx^2} = \varepsilon\Psi}$$

- Set of normalized eigenfunctions

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right), \qquad (1)$$

where $n = 1, 2, 3, \cdots$ and $L = b - a$ is the width of the box.

- Set of eigenenergies

$$\varepsilon_n = \frac{\pi^2 n^2}{2L^2} \qquad (2)$$

- Note that $\varepsilon_1 = 1$, $\varepsilon_2 = 4$, $\varepsilon_3 = 9$, $\cdots$ if $L = \frac{\pi}{\sqrt{2}}$.