1-d Schrodinger Equation -- Finding Bound states

Schrodinger Equation is a homogeneous Sturm-Liouville Problem

-- A linear and homogeneous BVP with no first derivative term

$$\psi(x,t) = u(x)e^{-iEt/\hbar}$$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + V(x)u = Eu$$

TISE

Dimensionless form

$$\xi = x/L$$

$$\frac{d^2u(\xi)}{d\xi^2} - (v(\xi) - \varepsilon)u(\xi) = 0 \quad ;$$

$$\varepsilon = \frac{2mL^2}{\hbar^2}E$$

$$v(x) = \frac{2mL^2}{\hbar^2}V(x)$$

Although u also has dimension -- it is not required to redefine it because
-- this is a homogeneous equation so dimensions of u cancel on both sides
-- if u(x) is a solution then any constnt times u(x) is also a solution

We can use Shooting method, finite difference method or Numerov method to solve Schrodinger Eq

Hurdles

1. The solution does not exist for all energies but only for some specific energies $E_{min} \leq E < E_{max}$
2. The wavefunction should approach zero as x approaches +(-) infinity $E_{min} = V_{min}$ → global min

   i.e. Correct asymptotoc solution

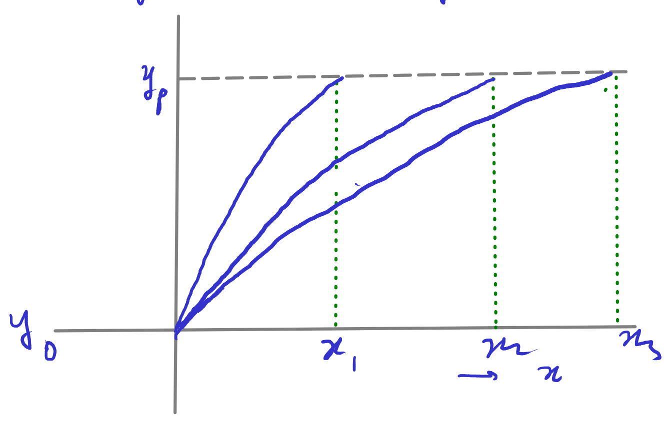
   -- How do define infinity?
3. Ensure continuity of wavefunction and its derivatives

BC at infinity

Three procedures for implementing boundary conditions at infinity

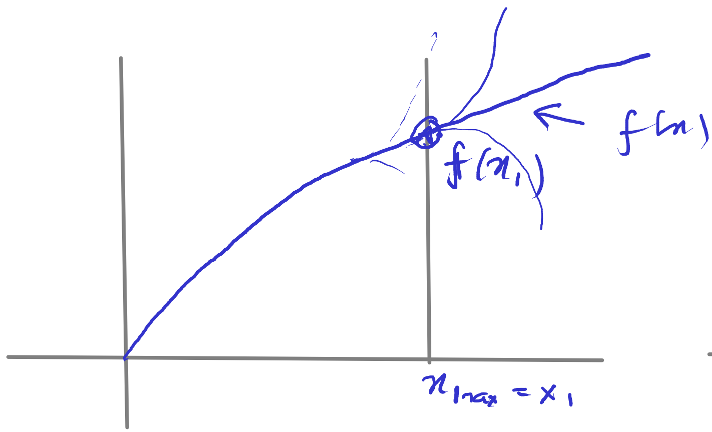
a) Replace ∞ with a large value of x (x = X_max)
b) Match an asymptotic solution at large values of x $\lim_{x \to \infty} y(x) = f(x)$ use $y(x_1) = f(x_1)$
c) Get an asymptotic expansion of your solution at the x=∞
   Start from the asymptotic solution at large x and integrate inwards

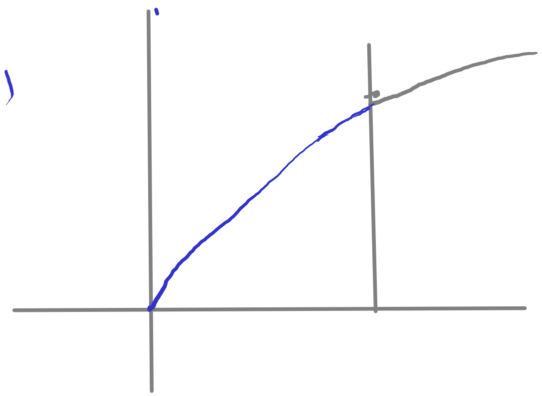
Let $y(x \to \infty) = y_f$ & $y(x=0) = y_0$



$x_{max} = \begin{cases} x_1 \\ x_2 \\ x_3 \end{cases}$

(a)

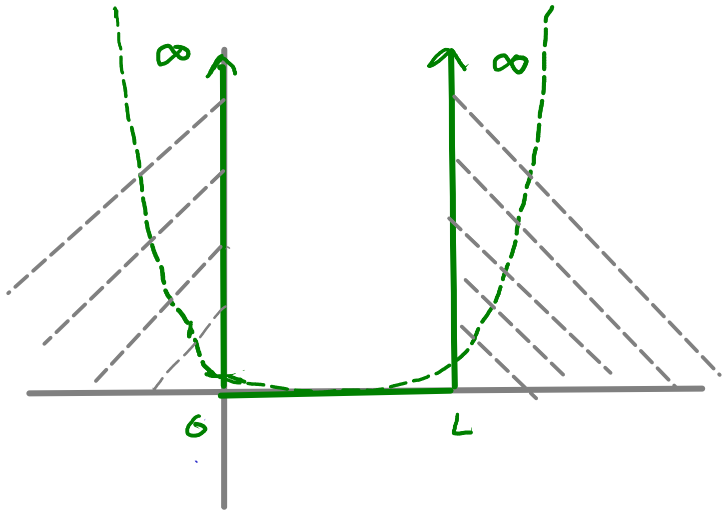




Shooting Method

Consider the problem of a particle in a square potential well of length L with infinitely high walls, i.e.

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{elsewhere} \end{cases}$$



$\rightarrow \quad \psi(x,t) = 0 \quad \text{at} \quad x = 0, L$

$$\xi = \frac{x}{L}$$

$\Rightarrow \quad u(0) = u(L) = 0$

Rewriting ξ as x , we are required to solve the BVP

$$u''(x) - (v(x) - \varepsilon)\, u = 0 \qquad x \in [0, 1]$$

with Dirichlet boundary conditions

$$u(0) = u(1) = 0$$

In shooting method, we convert it into a system of two first order IVP

$$\frac{du}{dx} = y$$

$$\frac{dy}{dx} = \frac{d^2u}{dx^2} = (v(x) - \varepsilon)\, u$$

What are the initial conditions?

We know $u(0) = 0$

In shooting method,

-- We guess the value of $y(0)$ (or $u'(0)$) say $y(0) = s$

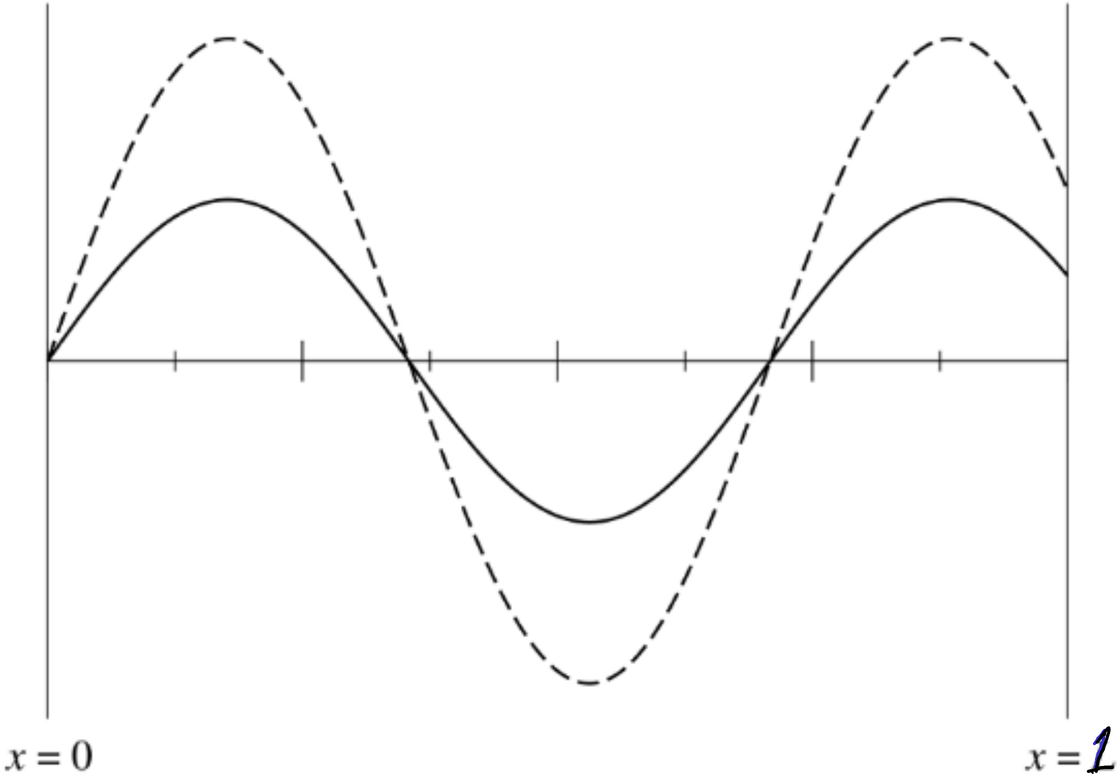
-- calculate the solution from x = 0 to x= 1 using some method used to solve IVP

e.g. 4th order Runge Kutta.

-- Require that the other boundary condition u(1) =0 is satisfied

i.e find roots of $\phi(s) = u_s(1) = 0$

the solution does not go to 0 at x=1



try to fix this by changing the initial condition on y(x) using a root finding method

This will not work!

If we just double the initial condition on y we get the dashed curve!

The initial condition only affects the overall magnitude ofthe solution, but does not change the shape.

This is because the equation is linear – if u is a solution, cu is also a solution

In fact for an arbitrary choice of ε , there is no solution that satisfies the boundary conditions

The solutions exists only for some specific/allowed valuesof ε – eigenvalues

To find the allowed values of energy – we use the shooting method but rather than changing the initial conditions, we vary ε

For a particular set of initial conditions, we vary ε to find the value for which u(1) = 0, But that leaves the inititial condition

Since changing this boundary condition, only changes the solution by a simple multiplicative factor, it doesn't matter what this is set to!

this factor is fixed by normalization of the wavefunction.

$$u_0 = u(0) = 0 \quad , u_1 , \quad u_2 , \quad \cdots \quad , u_{N-1} , \quad u_N = u(1) = 0$$

Simpson 1/3 $\quad \int_0^1 u^2 dx = \alpha \qquad u_{norm}(x_i) = \dfrac{u_i}{\sqrt{\alpha}}$

$x \in [0, 1]$, $h = \frac{1}{N}$ $N = 100$

$\xi \equiv x = 0, \frac{1}{N}, \frac{2}{N}, \ldots, \frac{i}{N}, \ldots, \frac{N}{N} = 1$

Analytical Solution

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \Rightarrow \varepsilon_n = n^2 \pi^2$$

$$u_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad , \quad u_n(\xi) = \sin(n\pi\xi)$$

unnormalised

HW

Trial

Take ① $\varepsilon = 8$ & $u'(0) = 1$ & apply shooting method

plot the normalised eqn solution

change $u'(0)$ again plot → repeat

Also plot the analytical sol → normalised

verify that $u(1) \neq 0$

compare plot with normalised analytical solⁿ

② Repeat for $\varepsilon = 11$

③ repeat it with $0.9\pi^2$ & $1.1\pi^2$

④ Fix $u'(0) = 1$ Take $\varepsilon = \pi^2$

& plot → verify that $u(1) = 0$

Using Shooting to determine eigenvalues

These eigenvalues represent the energy values for bound states of a particle of mass m confined in a box potential

$E_{min} = 0$

$E_{max} = 2\pi^2$

fix $u'(0) = 1$, $tol = 0.5 \times 10^{-10}$

make a loop for E-values

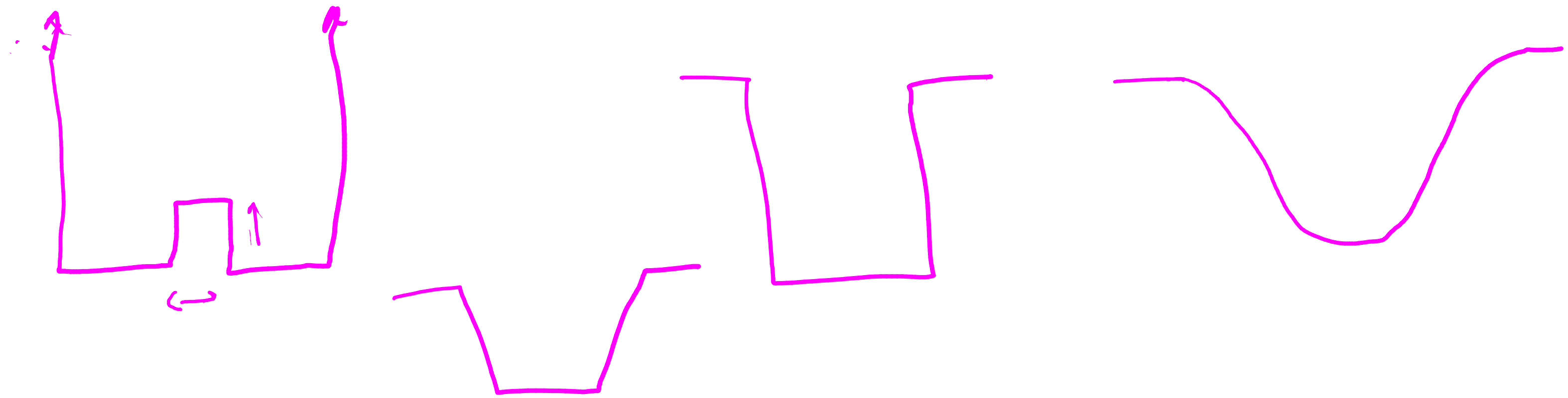
vary E between E_{min} to E_{max} with step size $De = 0.1$

use RK4 to determine u, print E, $u(1)$

till $|u(1)| < tol$

$E_{min} = 0.9\pi^2$, $E_{max} = 1.1\pi^2$, $De = 0.01$

0.001



First Approach

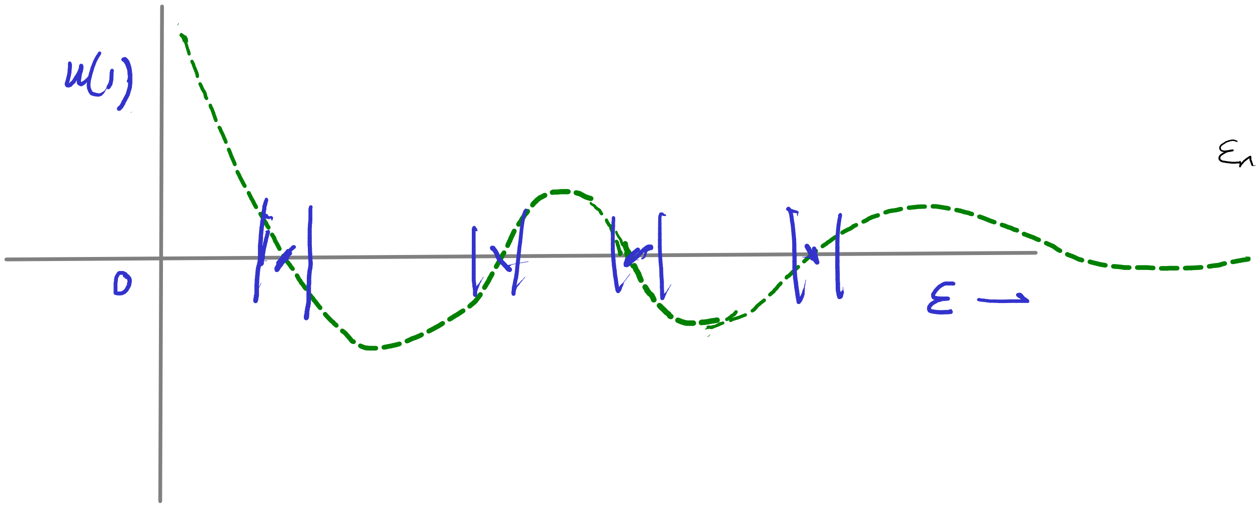
Need all energy eigenvalues bet $[0 : 200]$

$\Delta\mathcal{E} = 5$

$n^2\pi^2 = 200$

$n^2 \sim 20$

$n \sim 4$ or 5



$$\mathcal{E}_n - \mathcal{E}_{n-1} = n^2\pi^2 - (n-1)^2\pi^2$$
$$= (2n-1)\pi^2$$
$$= \pi^2 \text{ for } n=1$$
$$\sim 10$$

$u(1) \equiv u1$

$U(\mathcal{E}) = 0 \rightarrow$ solve it to find $\mathcal{E}$

Algorithm

1. Input x_{min}, x_{max}, NX (For pot well $x_{min} = 0$, $x_{max} = 1$ or $x_{min} = -\frac{1}{2}$, $x_{max} = \frac{1}{2}$)

2. $h = \dfrac{x_{max} - x_{min}}{NX}$, $x_i = x_{min} + i*h$

3. Define array v (in this case $v_i = 0$ for $i = 0, \ldots, N$)

4. $u_0 = 0$, $du_0 = 1$

5. Input E_{min}, E_{max}, (say $E_{min} = 0$, $E_{max} = 200$, NE

6. Compute $\Delta E = \dfrac{E_{max} - E_{min}}{NE}$ ($\rightarrow$ crucial)

ΔE E_{n+1} E_n actual

X

7. Make an array of E + $E_i = E_{min} + i*\Delta E$

8. input tole (tolerance for energy)

1-dim array of size = no of eigenvalues = m

9. call function eigenE to compute array. E_eig of energy eigenvalues

fn =

10. For each of the energy eigenvalues call RK4 routine to compute wavefn arrays $u_1[\,]$, $u_2, \ldots, u_m$ (m being no. of eigenvalues) len(x)

11. Call simpson to integrate $|u1|^2$, $|u2|^2$, ... $|u_m|^2$ and get normalised eigenfunctions $u_1(x_i) \rightarrow \dfrac{u_1(x_i)}{\sqrt{I_1}}$ $\int_0^1 |u_1|^2 dx = I_1$

12. Define analytical solution

13. Plot numerical and analytical functions

$\varepsilon_n = n^2\pi^2$, $\varepsilon_{n-1} = (n-1)^2\pi^2$

$\varepsilon_n - \varepsilon_{n-1} = (2n-1)\pi^2$

Algorithm for function "eigenE" to determine energy eigenvalues

1. For each value in array ε call RK4 routine to determine $uR := u(x_{max})$

$\varepsilon = (\varepsilon_{min}, \varepsilon_{min}+\Delta\varepsilon, \varepsilon_{min}+2\Delta\varepsilon, \dots \dots \varepsilon_{max})$

$uR(5) > 0$
$uR(6) < 0$
$uR(9) > 0$
$uR(13) < 0$

2. make an array uR (u at right boundary) for each ε

$\varepsilon[5] = \varepsilon_{min} + 5\Delta\varepsilon$

3. check for sign changes in uR and store the indices just before sign change occurs in array 'zeroes'

→ zeroes = [5, 8, 12, ...]

len (zeroes) = m → no of eigen values

6. Make an array "energy-guess" containing energy values at these indices

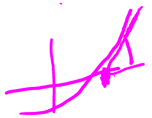
1-d array of size m

$\varepsilon[\text{zeroes}[2]] = \varepsilon[12]$

$f(x) = 0$

$\boxed{uR(\varepsilon) = 0}$

$\varepsilon[5], \varepsilon[6]$



7. For each of these guess values, call scipy.optimize.newton function to determine energy eigenvalues with accuracy tolE.
Note that for each computation in newton you have to again call RK4

8. Return the array containing these energy eigenvalues

$E \sim n^2$

Drawback: if the energy mesh is too coarse, or if the eigenvalues are very close, the probability to miss some eigenvalues is quite high

HW

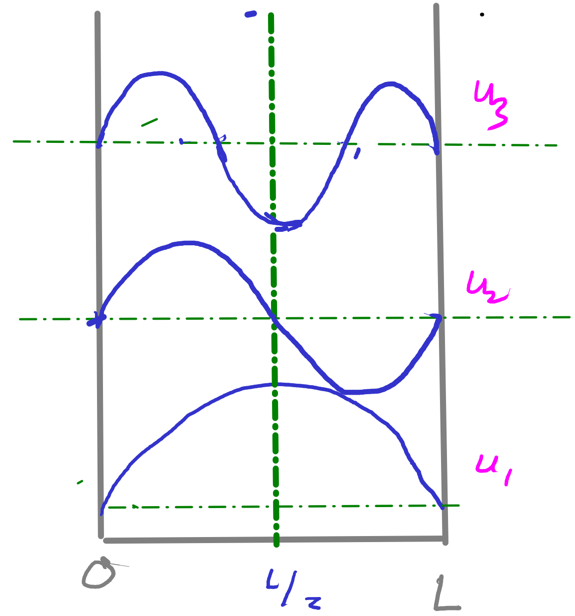
1) Obtain first ten energy eigenvalues for an electron in infinite pot well of width 5 angstrom
2) Plot ε as a function of n^2 and determine the slope. Compare with actual
3) Print a table of energy eigenvalues in eV along with the analytical values

n	E_{num}	E_{anal}

4) Plot first five normalised wavefunctions alongwith the corresponding analytical solutions
5) Plot the probability densities $|u|^2$ and show the verification that they are normalised wavefn

Second Approach

No of nodes in $u_n(x) = n-1$



$$u_n\left(\tfrac{L}{2}+x\right) = (-1)^n\, u\left(\tfrac{L}{2}-x\right)$$

No of nodes is given as input → n_nodes

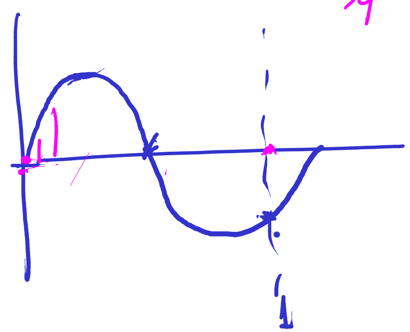
ε E_{max} E_{min}

E_{max} E_{min}

To find the interval E_{min}, E_{max}

Take $\varepsilon = \dfrac{E_{min} + E_{max}}{2}$, & solve eq^n & find no of

nodes in sol → n_c



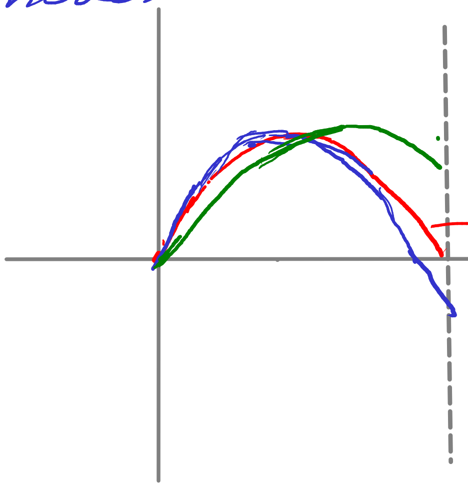
- if $n_c >$ n_nodes $\Rightarrow \varepsilon >$ actual ε
  replace E_{max} by ε & repeat
- if $n_c \leq$ n_nodes $\Rightarrow \varepsilon <$ actual ε replace E_{min} by ε
- repeat till $E_{max} - E_{min} <$ etol

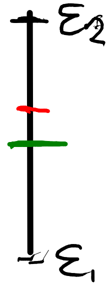
This gives a rough interval for each n. To find the numerically accurate solution:

say $n_{\text{nodes}} = 0$

$u(1) > 0$

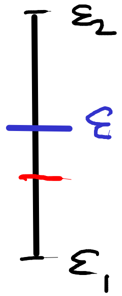
$\varepsilon < \varepsilon_{\text{actual}}$





update $\varepsilon_1 \to \varepsilon$

actual



$\varepsilon > \varepsilon_{\text{actual}}$

$u(1) < 0$

update $\varepsilon_2 \to \varepsilon$

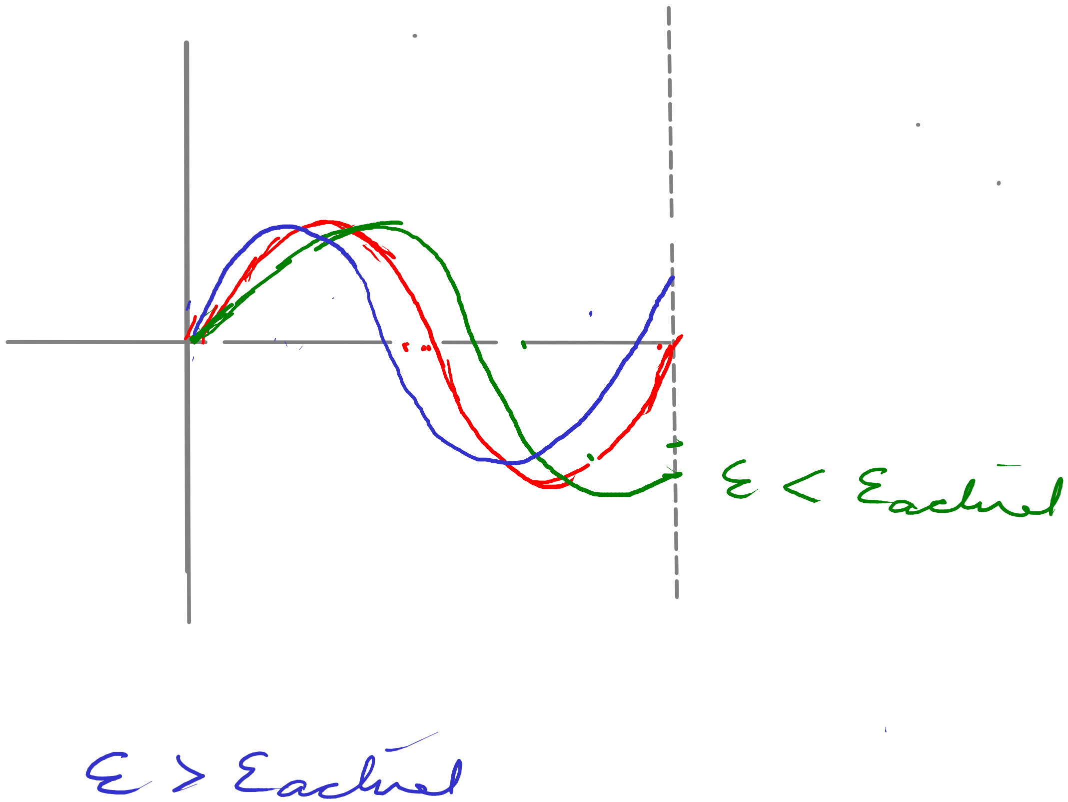
repeat till the interval $\varepsilon_{\max} - \varepsilon_{\min}$ is $<$ tol

10^{-10}

Similar when no of nodes is even

If n_nodes is odd

say n_nodes = 2



Repeat till $|u(1)| < ftol$ ↳ tol for wave fn.